PHYSICAL and STRUCTURAL PROPERTIES of BINARY SELENIDE GLASSES

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Chalcogenide glasses

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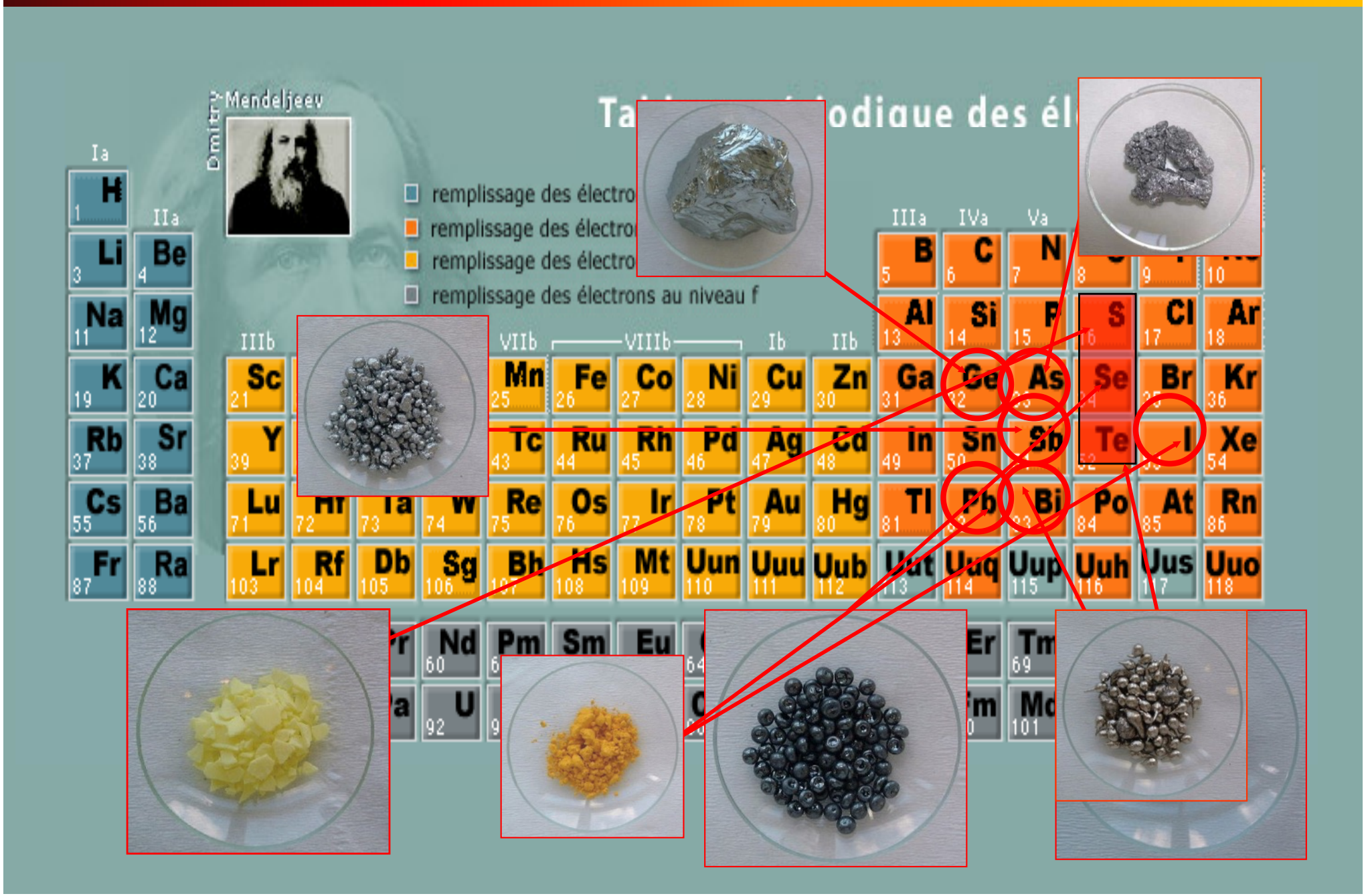

Chalcogenide glasses

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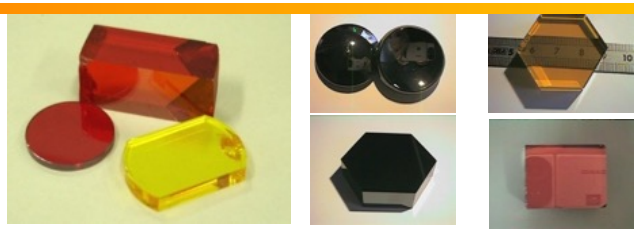
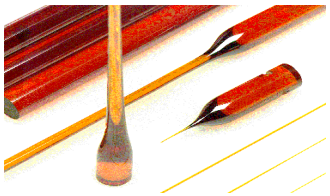
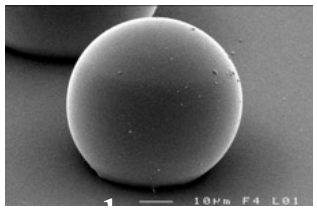
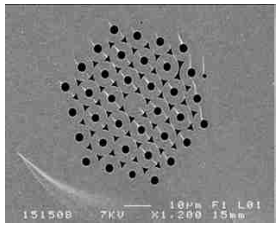
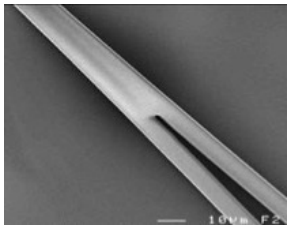
- **Large optical transparency from the UV to the far-infrared**



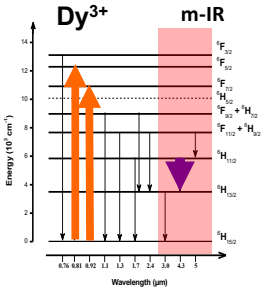
- **Thermo mechanical properties of glasses:**

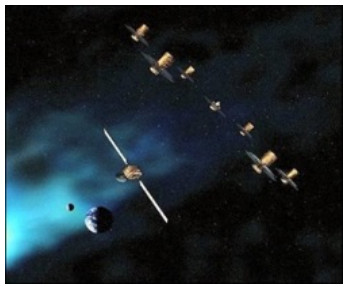
shape into optical fiber, planar guides, lenses, spheres…

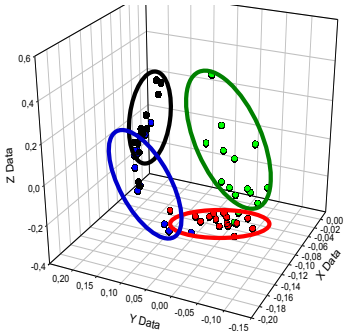




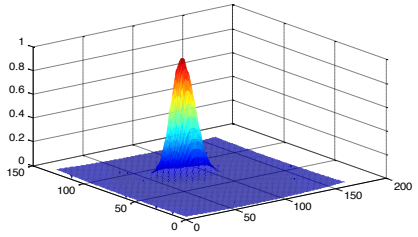
- **Potential applications**
  - Lasers sources
  - Space optics
  - Night vision camera
  - IR Sensing
  - thermoelectricity
  - Photoelectricity
  - DVD Technology
  - …





Pathologic states





Their structural organisation are not so well known,

Even for simple binary systems

Structure of Se and Te

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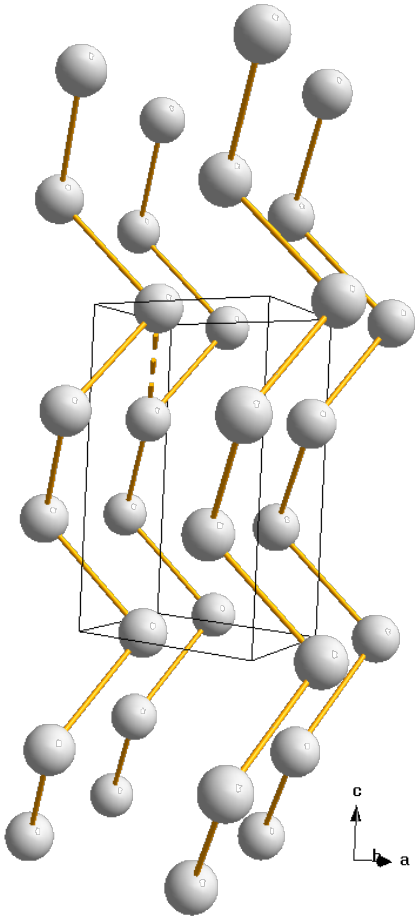
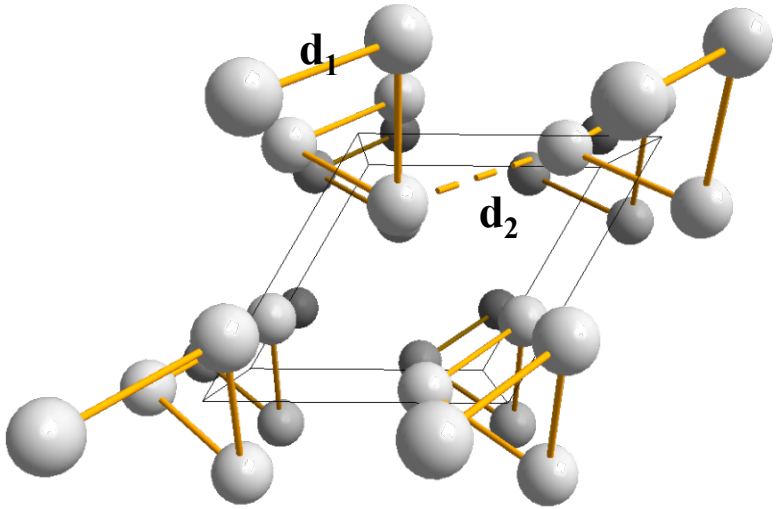
Se, Te: isotypic structures (Hex.)

- **Se → excellent glass former**
- **Te: not a glass former**

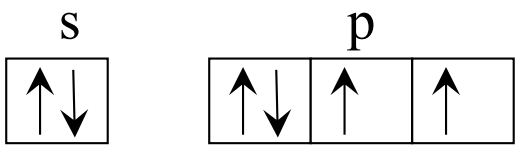




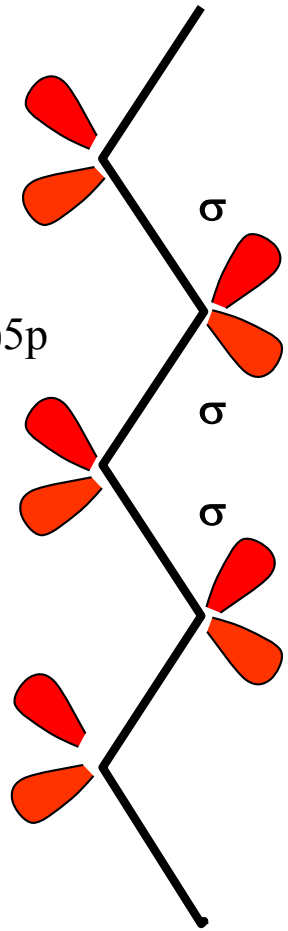
Se, Te

	d_1 (Å)	d_2 (Å)	d_2/d_1
Se	2.374	3.426	**1.443**
Te	2.834	3.491	**1.231**

Se crystal to glass



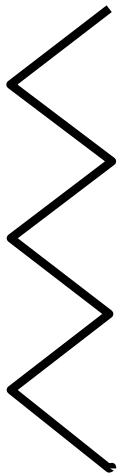
Groupe VI



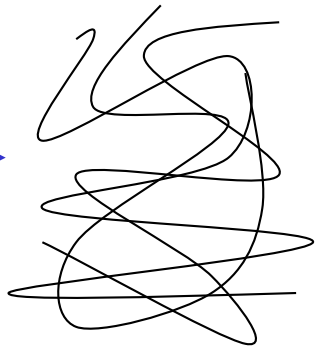
Localised (4e$^-$)5p

Lone pairs

Se chains :
easy rotation
and bending



Crystal



Glass

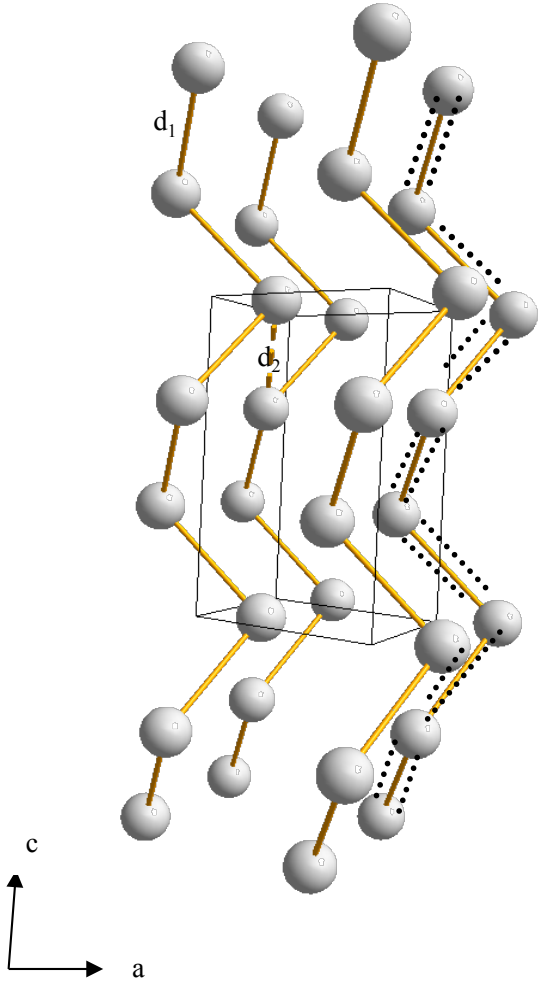
Se melting : 217°C

Viscous liquid

Easy glass forming

Te structure and bonding

Crystalline structure of metallic Te



π metallic bonding

	d_1 (Å)	d_2 (Å)	d_2/d_1
Se	2.374	3.426	**1.443**
Te	2.834	3.491	**1.231**

RIGIDITY

- Pure Te → no glass
- Te is not a glass former
- Tm = 450°C, fluid melt

seven order of magnitude in conductivity between Se and Te

Se : a key atom in chalcogenide glass

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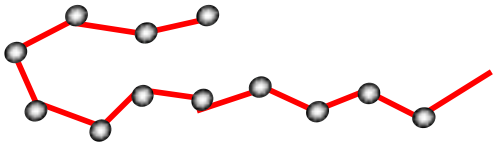
- Good glass former
  - low phonon characteristics
  - technical glasses such as AMTIR (Amorphous materials Inc)
  - GASIR (Umicore IR Glasses) based on combination of Se, Ge, As, Sb.
  - TAS (Te/As/Se) DIAFIR

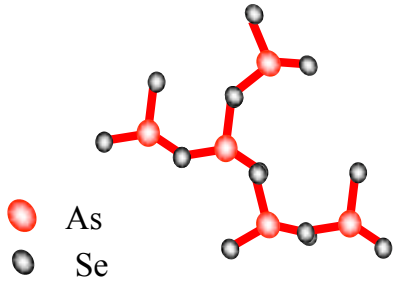
- local probes for NMR spectroscopy

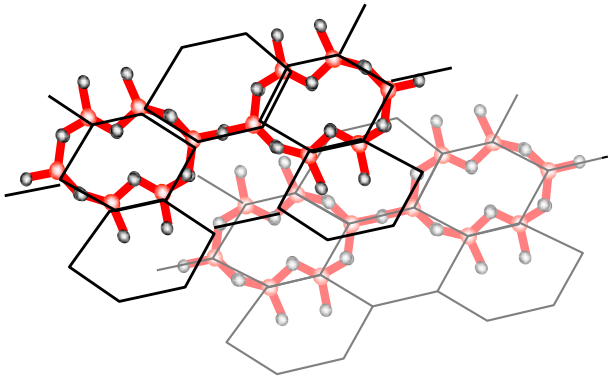
Se chain reticulation

1) 1D spaghetti-type, such as vitreous Se

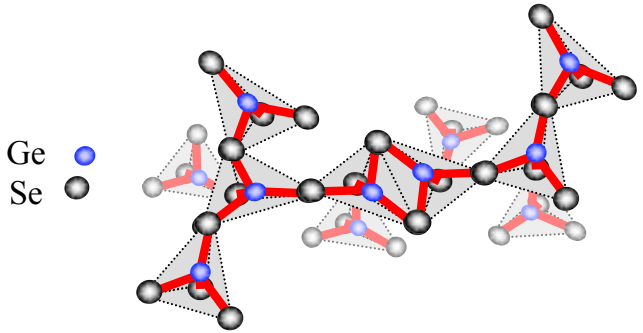


2) 2D distorted planar glasses such as As_2Se_3





3) 3D glasses, such as $GeSe_4$



Binary As-Se and Ge-Se systems

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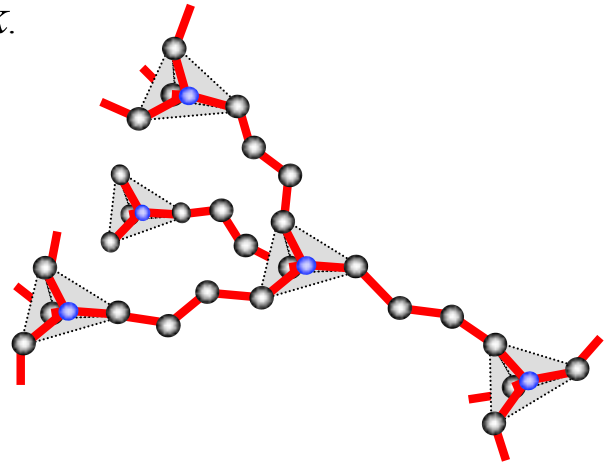
Network built with $AsSe_3$ pyramids or $GeSe_4$ tetraedra

"chains crossing model":

As and Ge atoms are homogeneously distributed on the network.

⇒ the polyedra are linked by Se chains

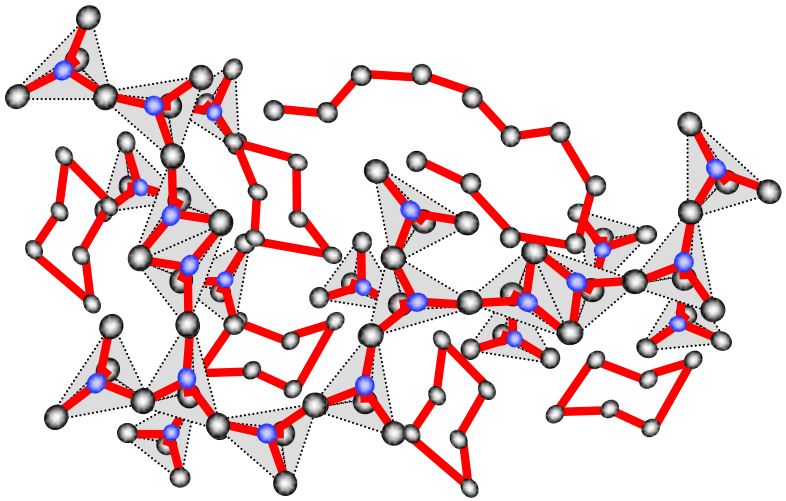
⇒ Se chains have the same length.



"Clustering model" :

⇒ Cluster rich in shared polyedra

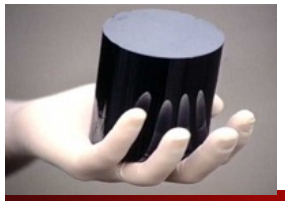
⇒ The "excess" of Se form chains or rings



"random distribution":

⇒ In between the above extreme situations

⇒ polyedra and Se chains are randomly distributed



Study of the As_xSe_{1-x} binary system

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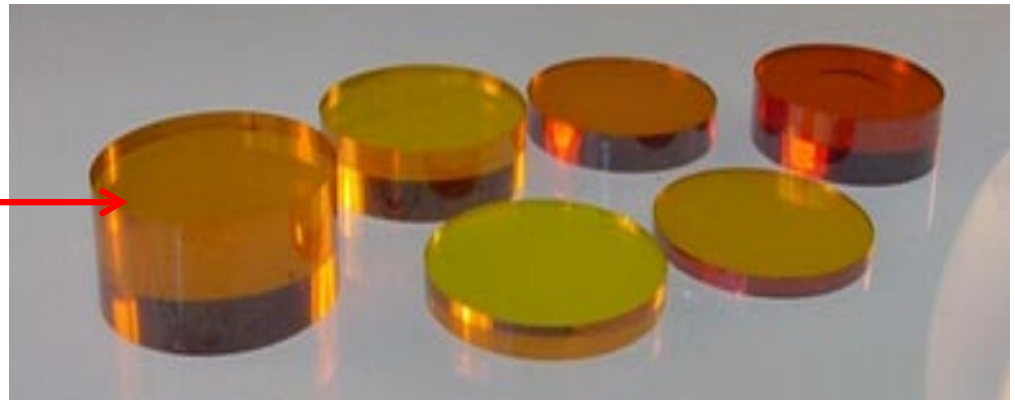
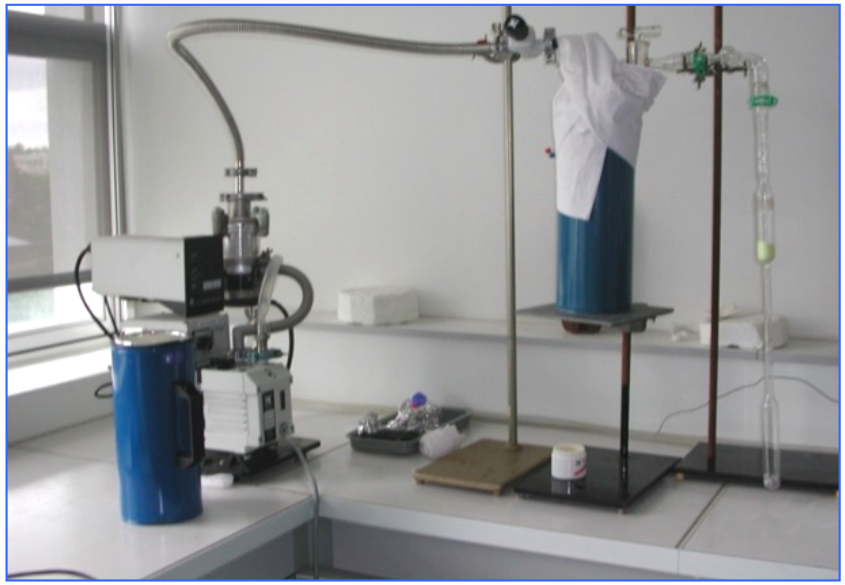
In the range 0 <x< 0.4, from Se to As_2Se_3,
previous investigations are consistent indicating that the As_xSe_{1-x} glass structure follows the CCM.

In the range 0.4 <x< 0.6 from As_2Se_3 to As_3Se_2,
It is less clear. Some previous studies suggest that the structure follows the CCM assuming that the glass network progressively become more and more over constrained with As-As bonds. Other authors suggest the existence of cages.

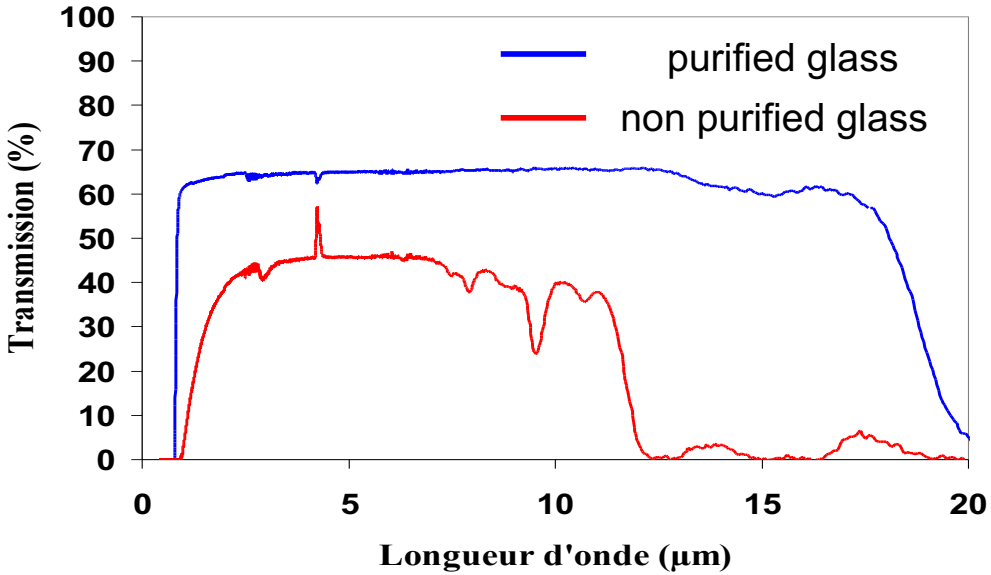
Let us discuss the physical and structural properties of a **unique set of glasses**

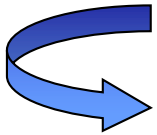


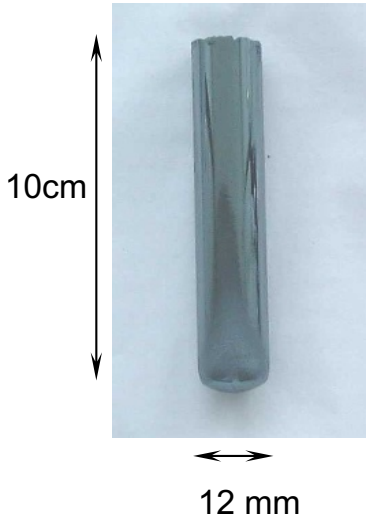
Chalcogenide glass synthesis

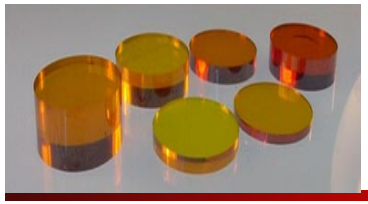


- High purity elements (5-6N)
- Under vacuum (10^{-4}-10^{-5}mbar) in a silica set-up
- Purification processing
  - Chalcogenide distillation
  - Glass distillation
  - Oxides and hydrogen getters (Al, $TeCl_4$)
- Thermal treatment: rocking furnace at 700-900°C-10h
- Quenching and annealing

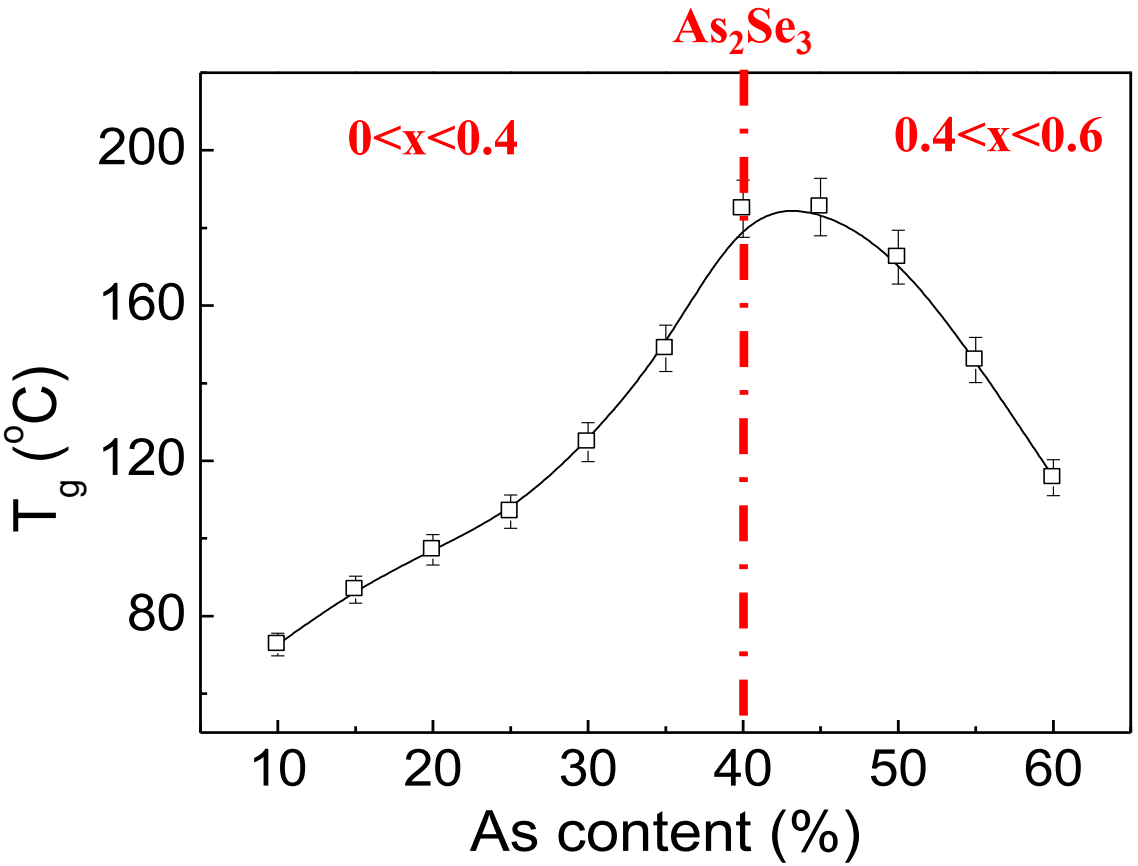






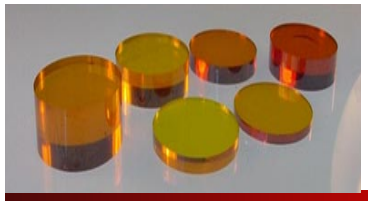


Glass transition temperature -T_g

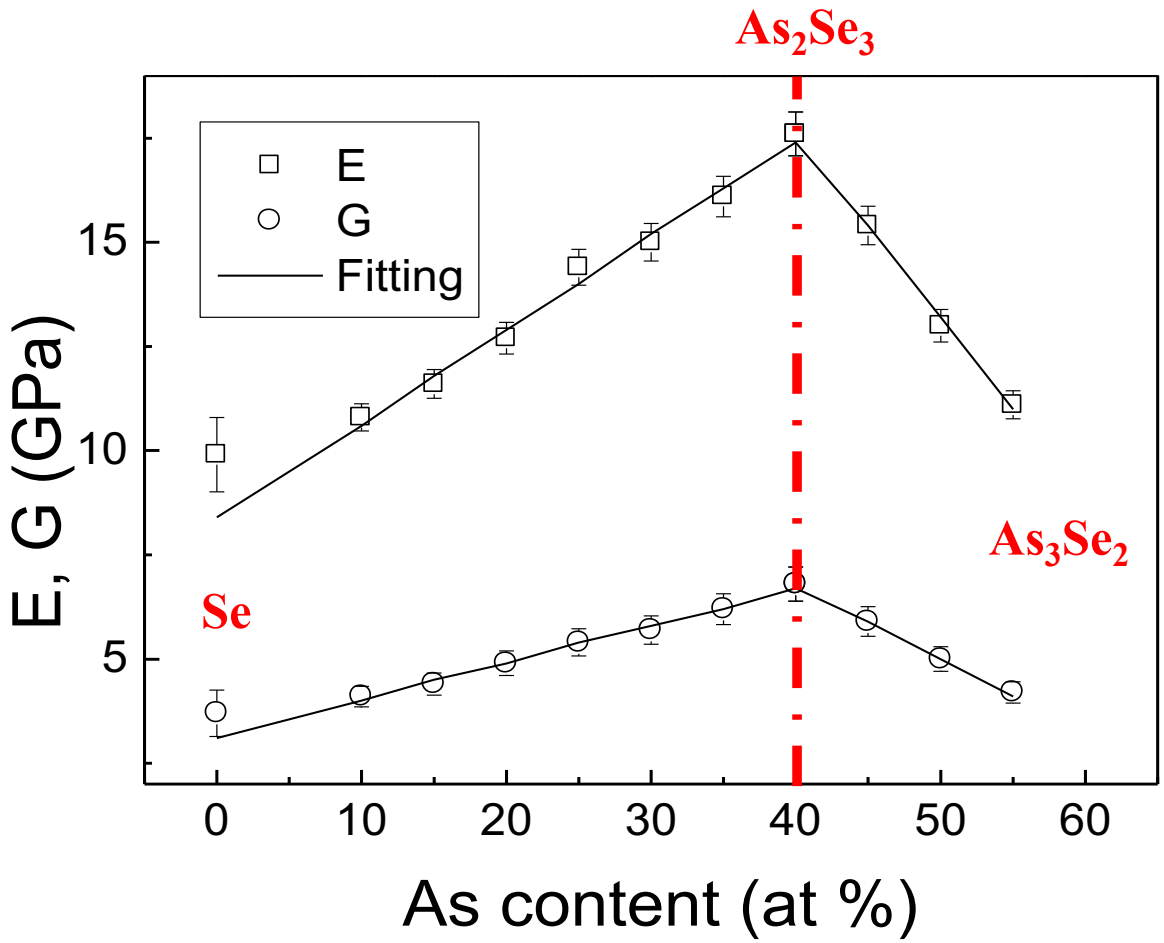


• **0<x<0.4**, the increase of T_g agrees with the increase of the reticulation of the network according the CCM.

• **0.4<x<0.6**, the decrease of T_g also agrees with the existence of As-As weaker homopolar bond in the CCM.



Young's and shear moduli -E and G



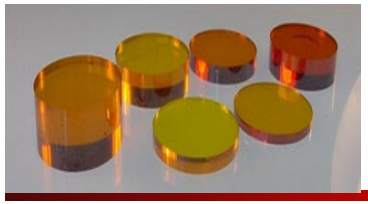
$$E = \rho\,(3\,V_l^2 - 4\,V_t^2)/((V_l/V_t)^2 - 1)$$

$$G = \rho\,V_t^2$$

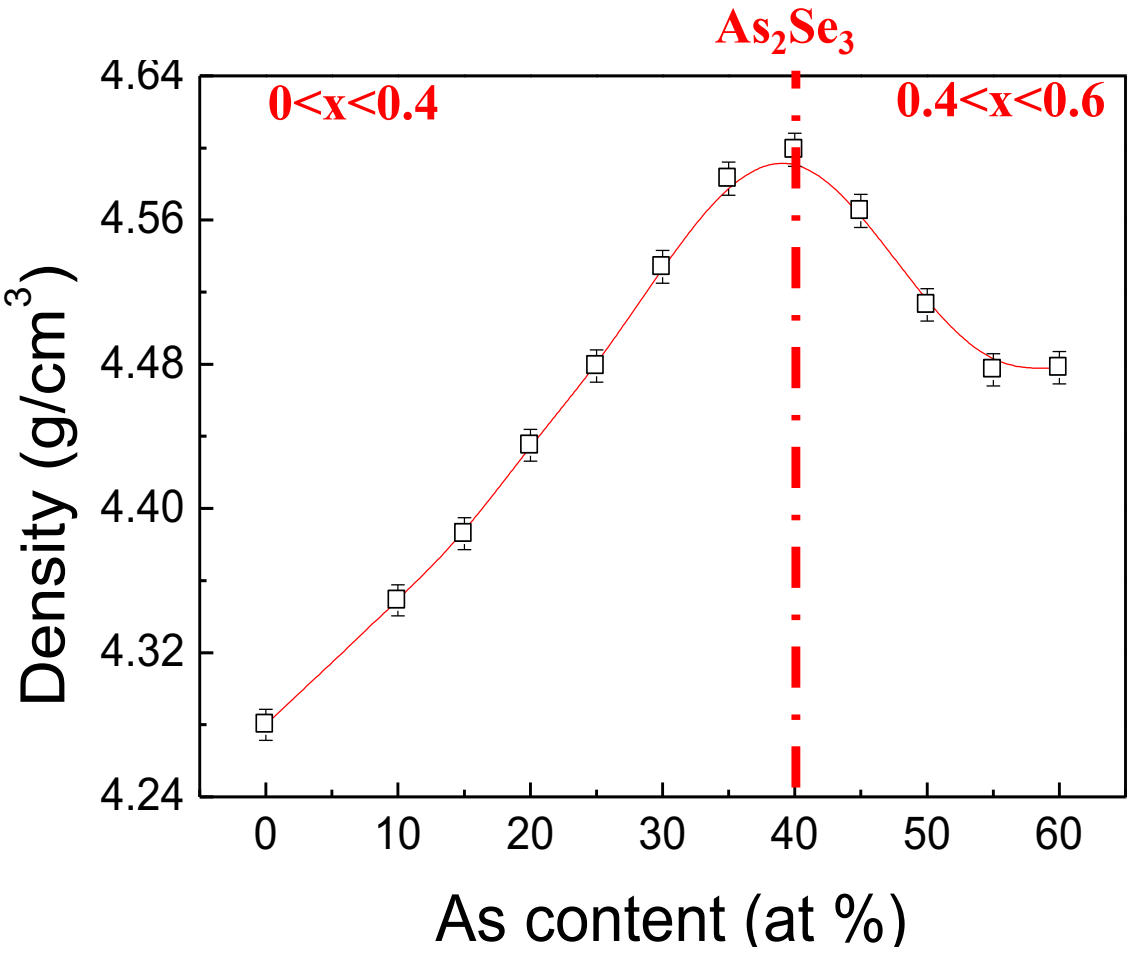
Elastic moduli calculated from the longitudinal (V_l) and transverse (V_t) ultrasonic wave velocities with a piezoelectric transducers.

E and G are related to the density of the mean bonding energy

The maxima at x= 0.4, are in agreement with the T_g changes

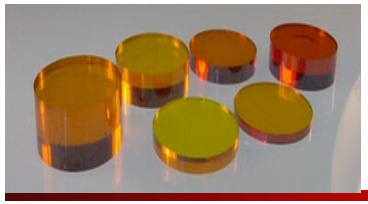


Density- ρ

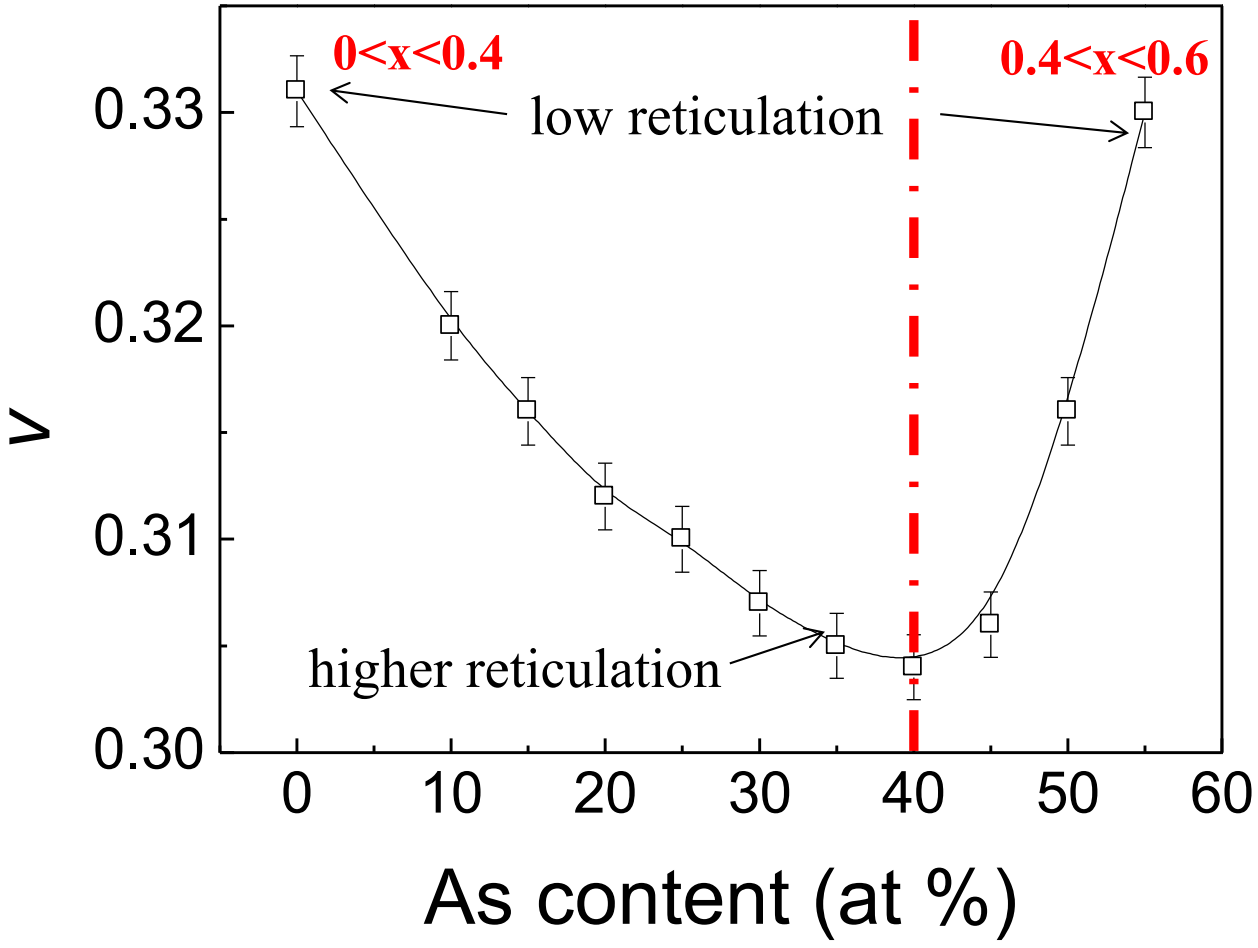


• **0<x<0.4,** the increase of ρ agrees with the increase of structural reticulation following the CCM.

• **0.4<x<0.6**, one would have rather expected a growth of ρ with the CCM with the higher content of threefold coordinated As.



Poisson's ratio-*v*



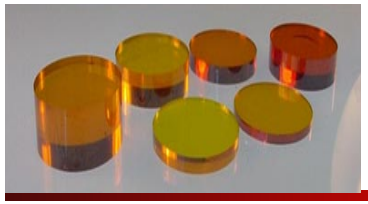
$\nu = E/(2G)-1$

ν gives account of the reticulation of glass network

[T. Rouxel, Phys. Rev. lett. (2008)]

• **0<x<0.4**, the decrease of ν agrees with the increase of structural reticulation following the CCM

• **0.4<x<0.6**, the increase of ν clearly disagrees with the CCM which predicts a continuous increase of the reticulation beyond x=0.4



Tg, density and elastic moduli

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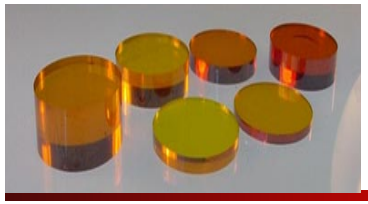
- T_g, density and elastic moduli of As_xSe_{1-x} glasses exhibit an extremum at $x = 0.4$ (corresponding to r=2.4)

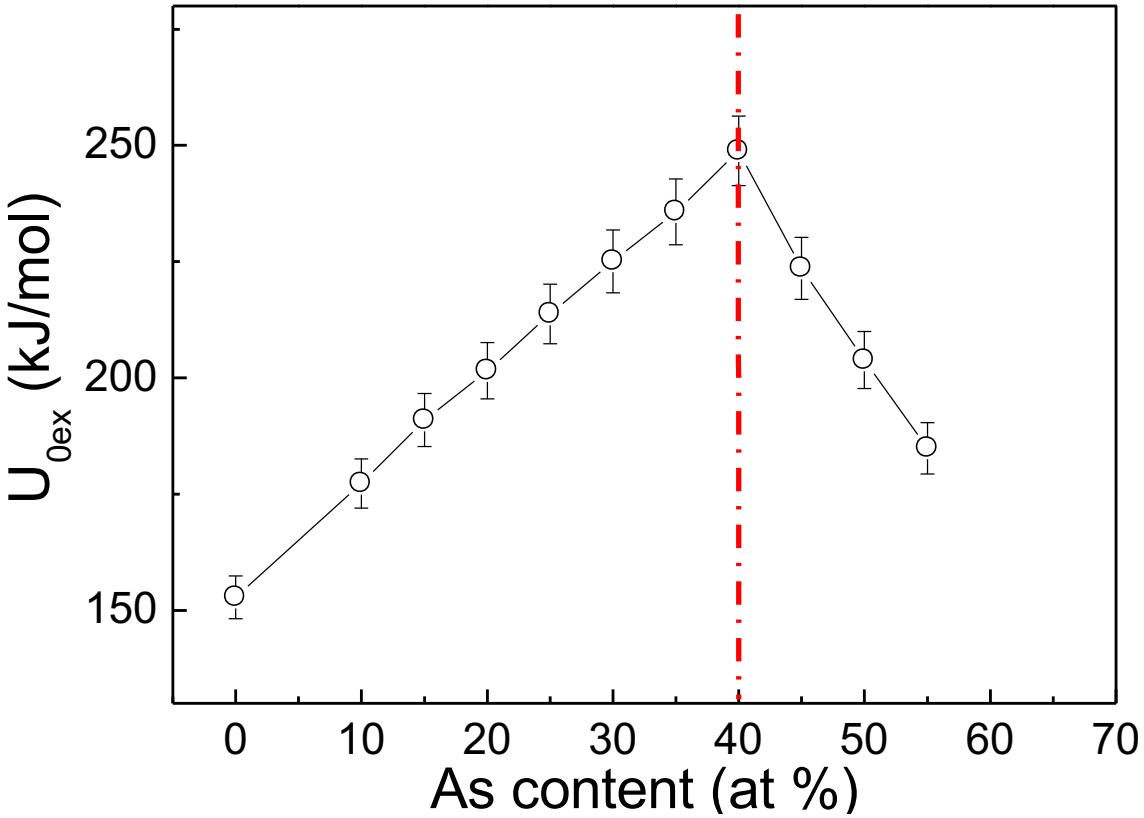
- The increases of this physical properties from x=0 to x=0.4 are in agreement with the CCM which is commonly *assumed* to describe these glass structures.

- The decreases of this physical properties for x>0.4 has to be explained. In particular the decreases of the density and the Poisson ratio are not consistent with the CCM.

- These properties are typically connected to the bonding energy and the network reticulation.



Experimental mean bonding energy-U_{0ex}

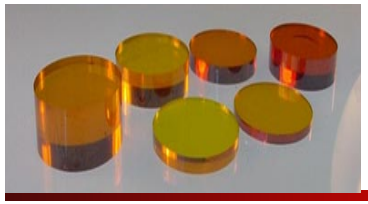


$$U_{0ex}=9EV_0/(3m_1n_1(1-2v))^*$$

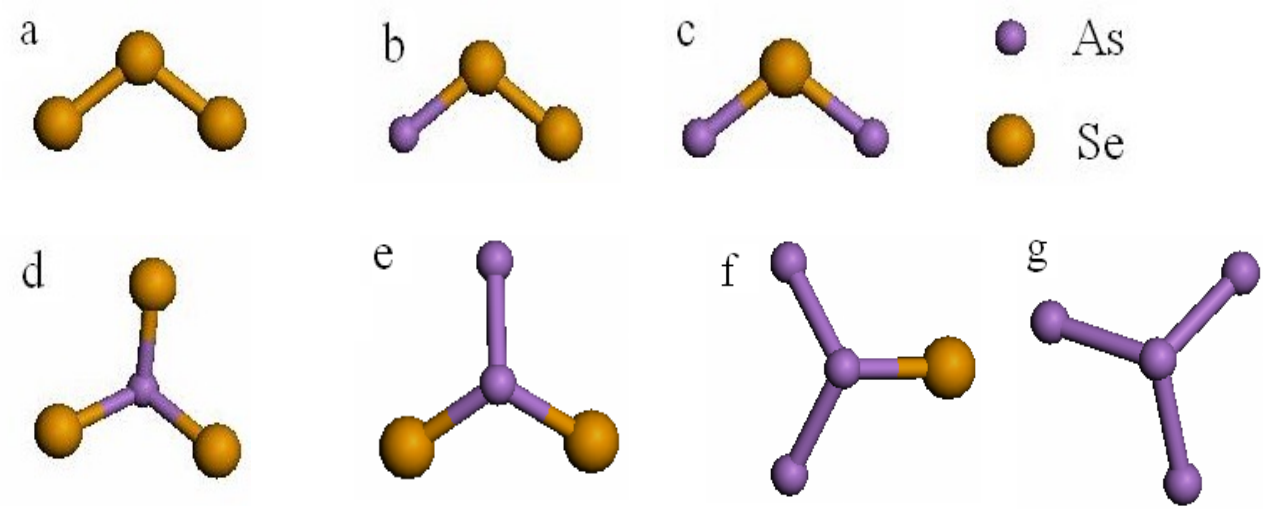
[T. Rouxel, C. R. Mec. **334**, 743 (2006)]

Finally, the experimental mean bonding energy changes follow the same trend than the elastic moduli

*V_0 is the atomic volume at equilibrium, m_1 and n_1 are the exponents of the power law describing the attractive and the repulsive terms. $m_1n_1/9 \approx 1$ in chalcogenide glasses



calculated mean bonding energy-U_{0th}



Three types of Se.

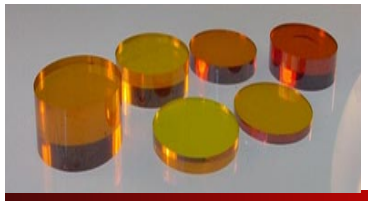
Four types of As

According to the Chain Crossing Model, theoretical U_0:

$0<x<0.40$, $U_0 = U_{Se\text{-}Se} + (3\,U_{As\text{-}Se} - 2.5\,U_{Se\text{-}Se})\,x$;

$0.40<x<0.60$, $U_0 = 2U_{As\text{-}Se} - U_{As\text{-}As} + (2.5\,U_{As\text{-}As} - 2\,U_{As\text{-}Se})\,x$.

For further explanation on the calculation : [**G. Yang et al., Phys. Rev. B. 82, 19 (2010)**]



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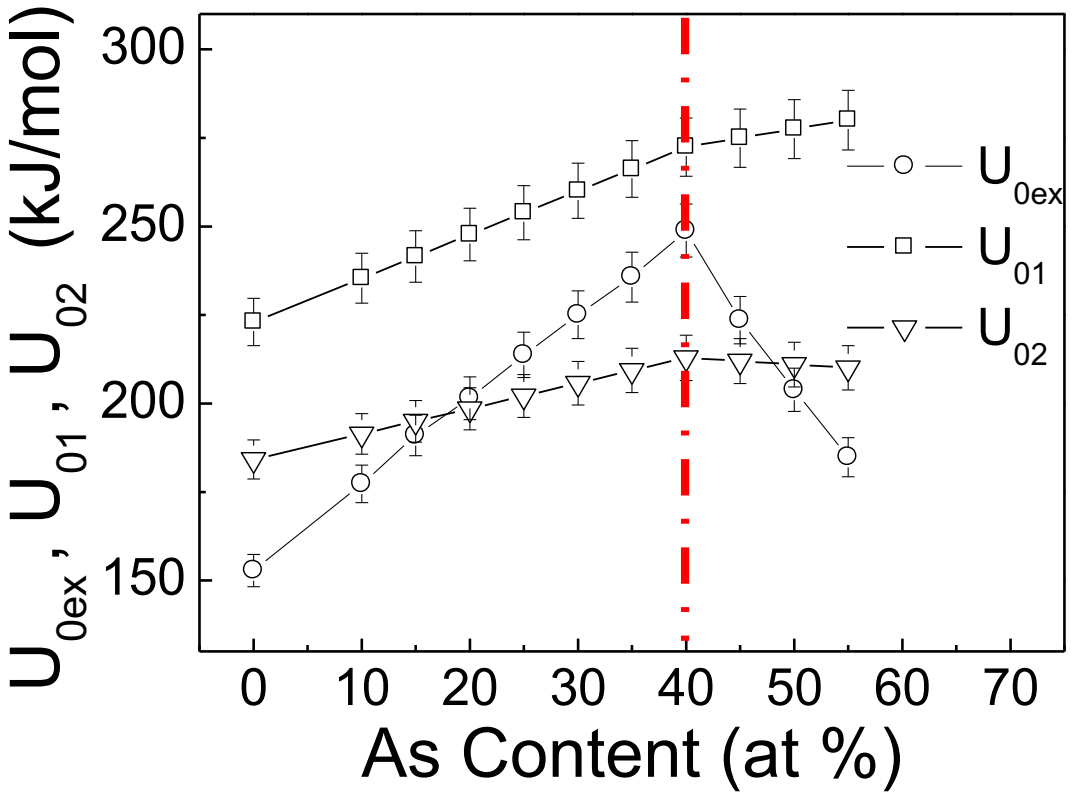


U_{01} = 223+123.5x kJ/mol ($x \leq 0.40$)
U_{01} = 252+51x kJ/mol ($x > 0.40$)

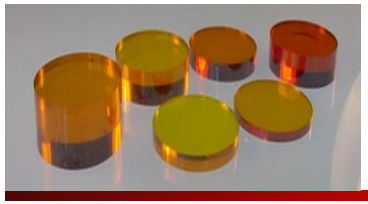
[E. V. Shkol'nikov, Sov. J. Glass Phys. Chem. **11**, 40 (1985)]

U_{02} = 184.2+71.74x kJ/mol ($x \leq 0.40$)
U_{02}= 220.5-18.87x kJ/mol ($x > 0.40$)

[L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, NY, 1960)]

- **0<x<0.4**, the CCM enables to give account of the experimental increase of the mean bonding energy

- **0.4<x<0.6**, the calculation based on the CCM including As-As bonds do not able to give account of the decrease of the mean bonding energy

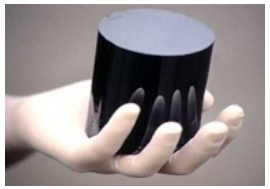


Mean bonding energy

The mean bonding energy calculation based on the **CCM is in a good agreement** with the evolution of the physical properties **from x=0 (Se) to x=0.4 (As_2Se_3).**

On the other hand, the same calculation **fails to explain** the physical behavior of the **glasses with x>0.4**, especially the density and the poisson's ratio.

To better understand the structure of this glass **^{77}Se NMR** experiments have been carried out and will be discussed in the following sections.



^{77}Se NMR in solid state materials

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	spin	Resonance frequency (MHz)	Natural abundance (%)	Absolute sensibility
^{77}Se	**1/2**	**57.3**	**7.6**	**$5.25.10^{-4}$**

- Signal broadening by Chemical Shift Anisotropy and disorder

  ⇒ Hahn spin full echo sequence

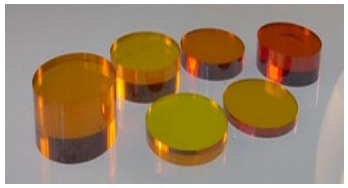
- Long spin-lattice relaxation time

  ⇒ Recycle time equal to 30 s

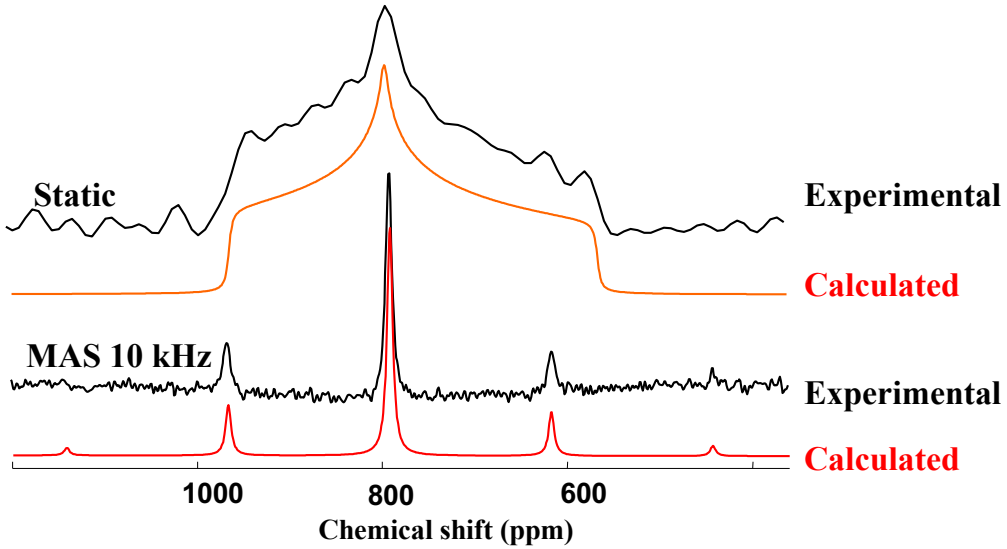
- Low sensibility

  ⇒ Up to 10000 scans

time consuming experiments (up to 80 hours)



^{77}Se NMR in the crystalline pure selenium



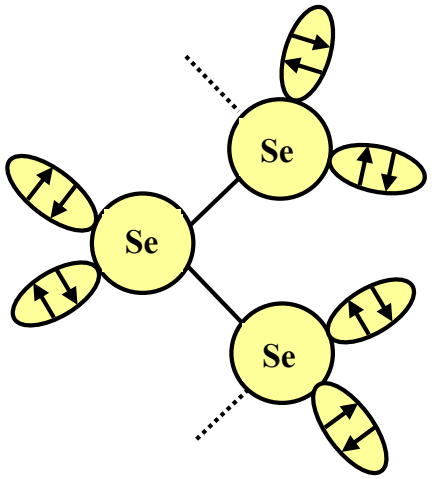
$$\delta_{iso} = \frac{1}{3}\left(\delta_{xx} + \delta_{yy} + \delta_{zz}\right) = \mathbf{792\ ppm}$$

$$\delta_{aniso} = \delta_{zz} - \delta_{iso} = -250\ \text{ppm}$$

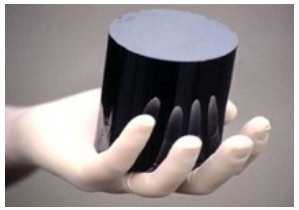
$$\eta = \frac{\delta_{yy} - \delta_{xx}}{\delta_{aniso}} = 0.8$$

Coherent with the structural data :

- a unique Se crystallographic site (792 ppm),
- with a complex local symmetry.



Confirmed our ability to record some reliable ^{77}Se spectra in solid state materials



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Solid State Sciences 5 (2003) 219–224

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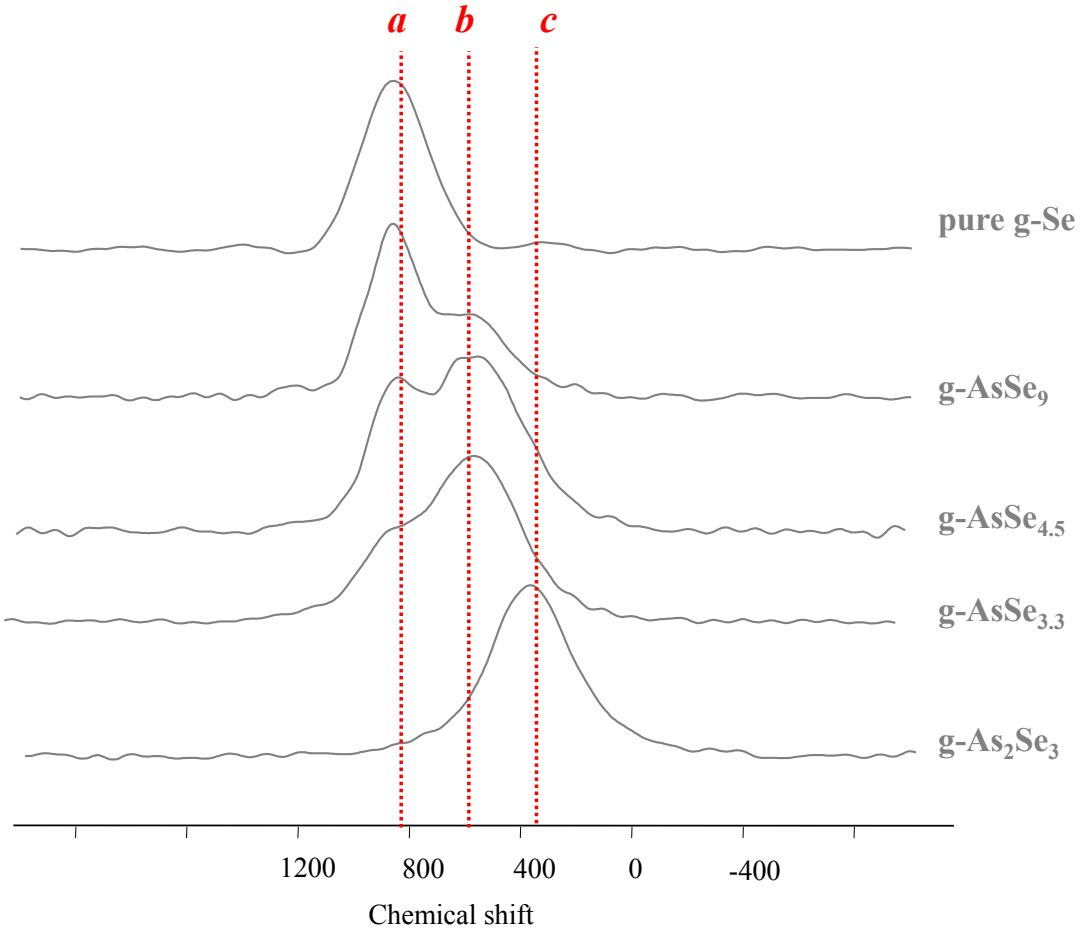
Solid state ^{77}Se NMR investigations on arsenic-selenium glasses and crystals

Bruno Bureau [a,*], Johann Troles [a], Marie LeFloch [a], Frédéric Smektala [a], Gilles Silly [b], Jacques Lucas [a]

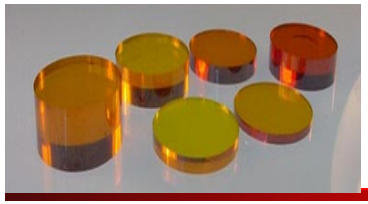


Three types of line are evidenced at

850 ppm (*a* lines)

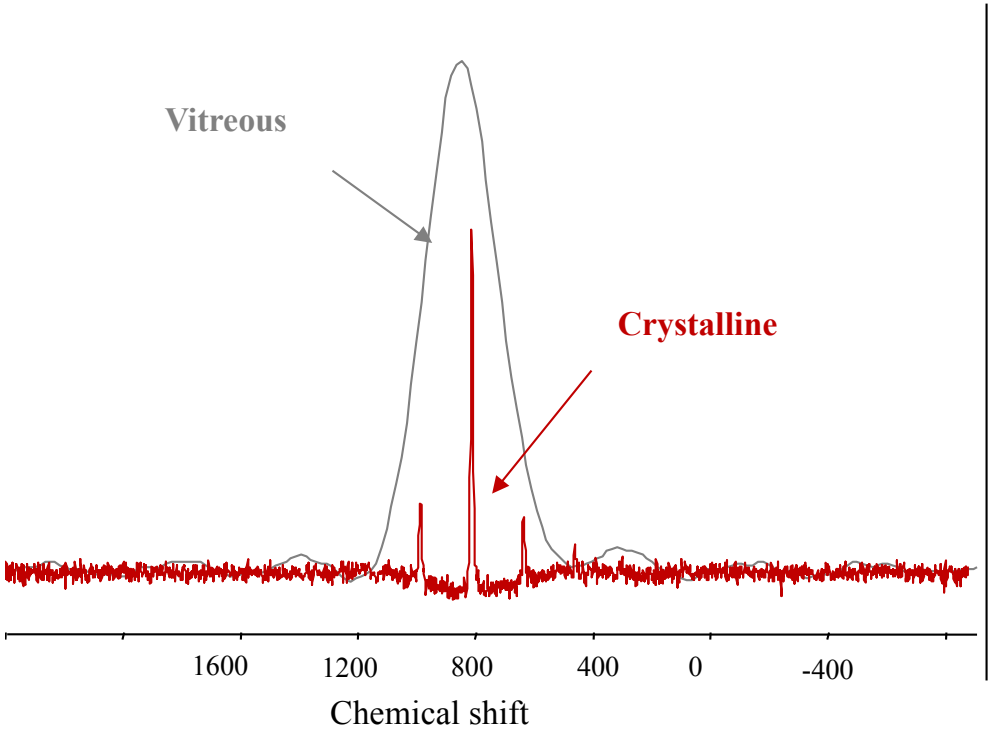
550 ppm (*b* lines)

380 ppm (*c* lines)



Assignment of the NMR lines

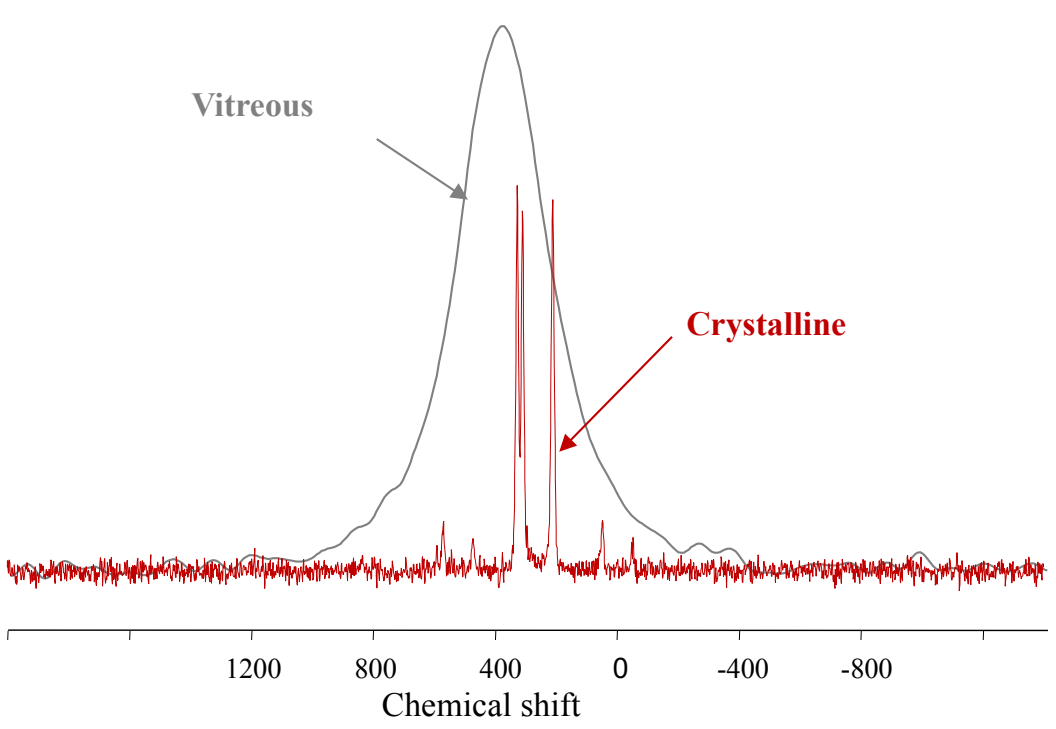
Vitreous and crystalline pure Se



⇓

a lines attributed to Se-**Se**-Se

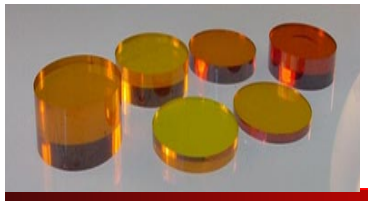
Vitreous and crystalline As_2Se_3



⇓

c lines attributed to As-**Se**-As

⇒ *b* lines attributed to As-**Se**-Se



"Chains crossing model" in As_xSe_{1-x}

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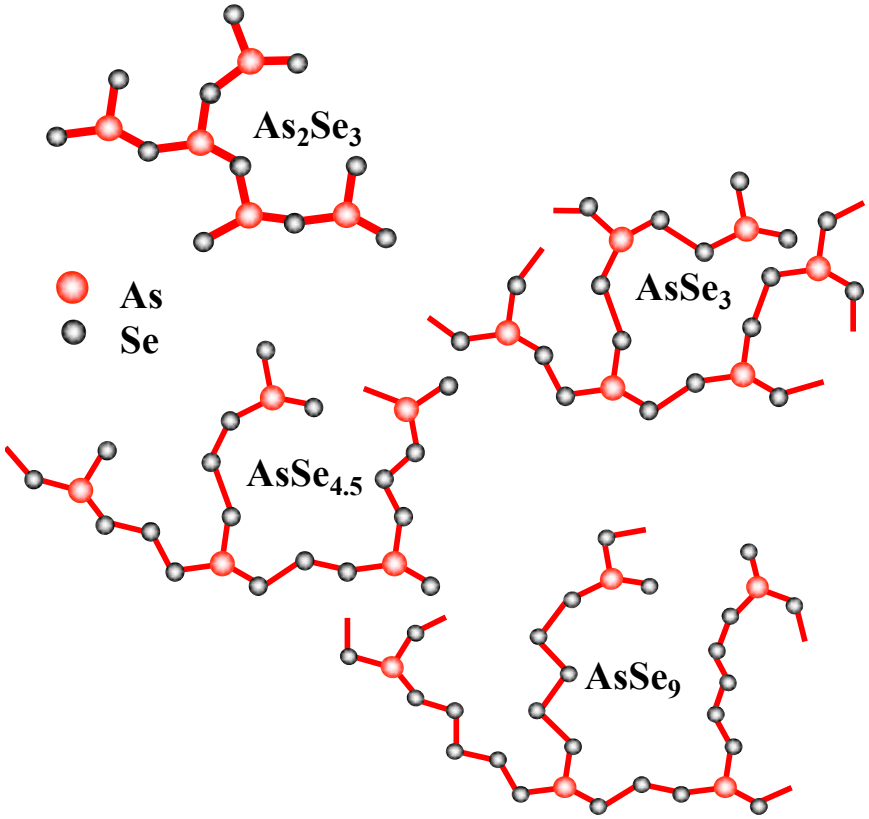
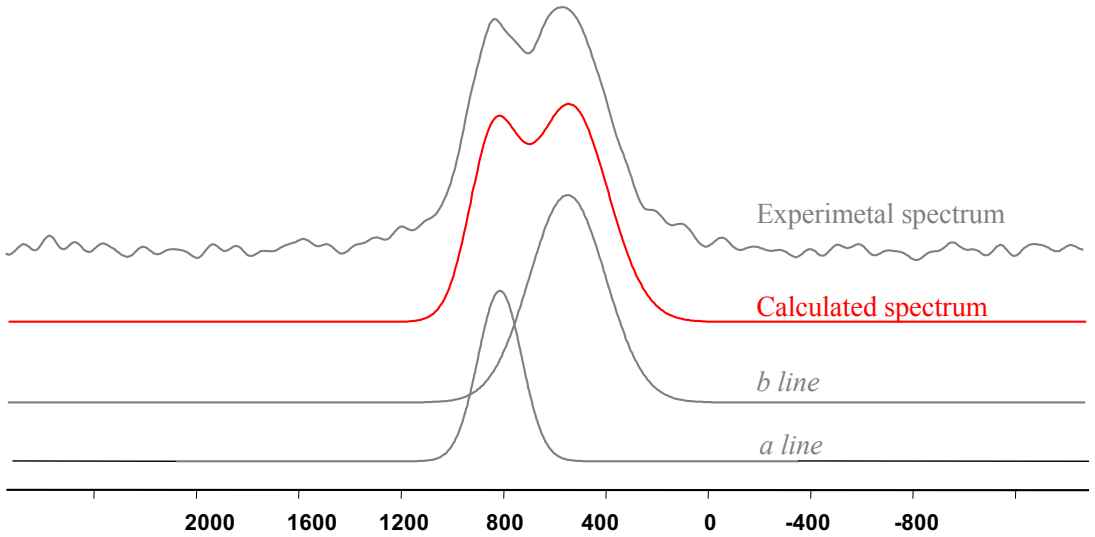
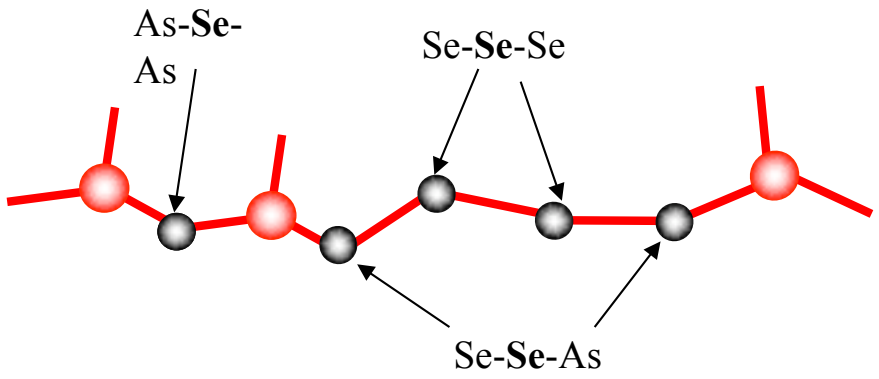


$AsSe_{4.5}$ spectrum reconstruction

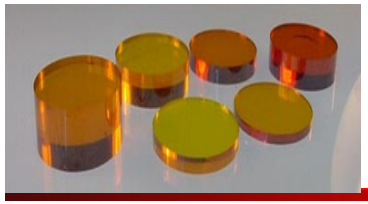


⇓

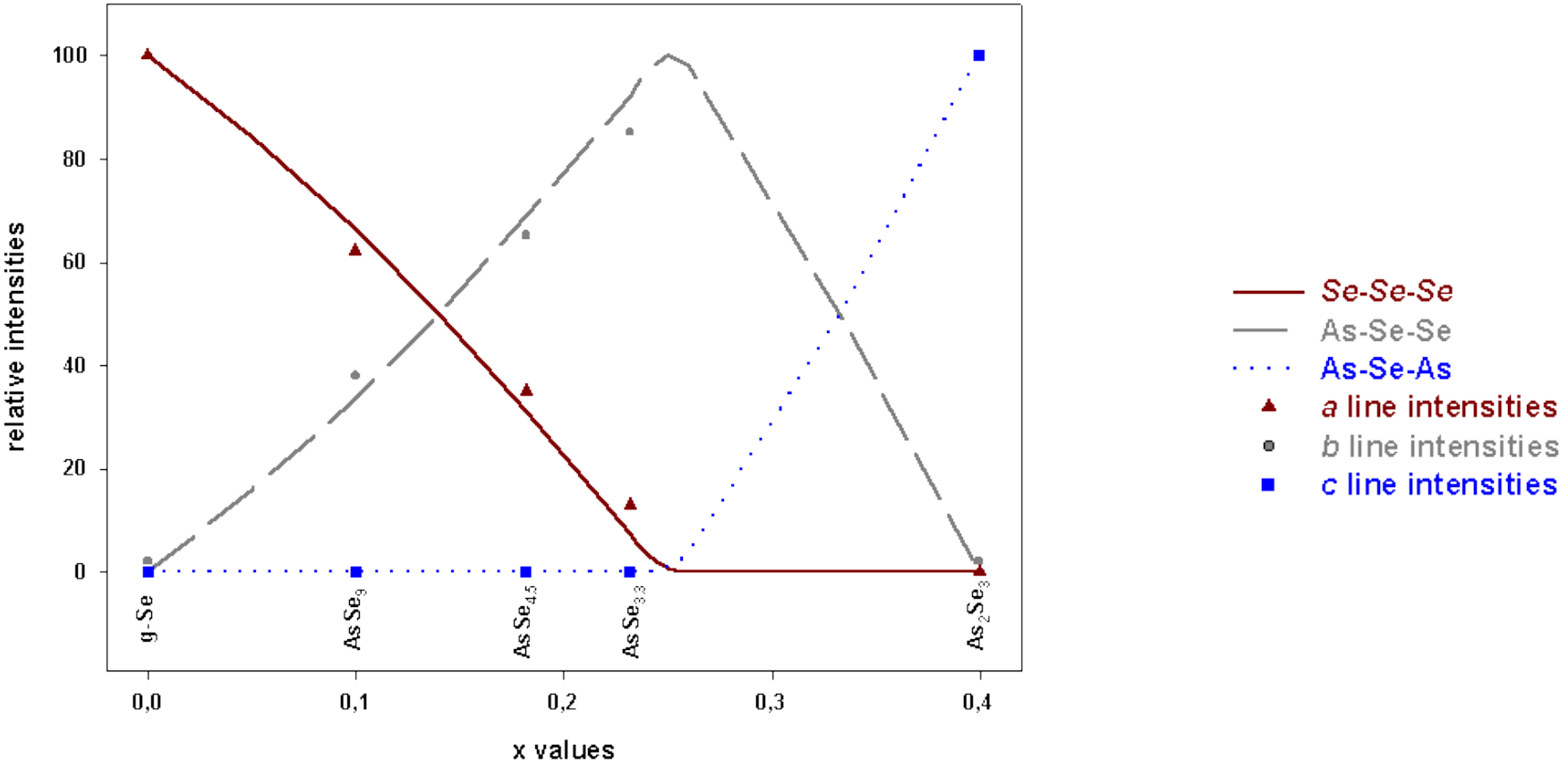
a, *b* and *c* line integrated intensities



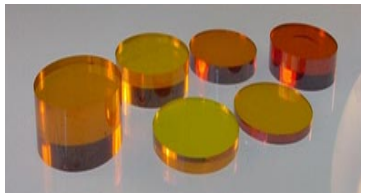
⇒ As-**Se**-As, Se-**Se**-Se, As-**Se**-Se rates



"Chains crossing model" in As_xSe_{1-x}



The ***a***, ***b*** and ***c*** line intensities fit well the, **Se-Se-Se**, **As-Se-Se**, **As-Se-As** rates expected with the "chains crossing model".

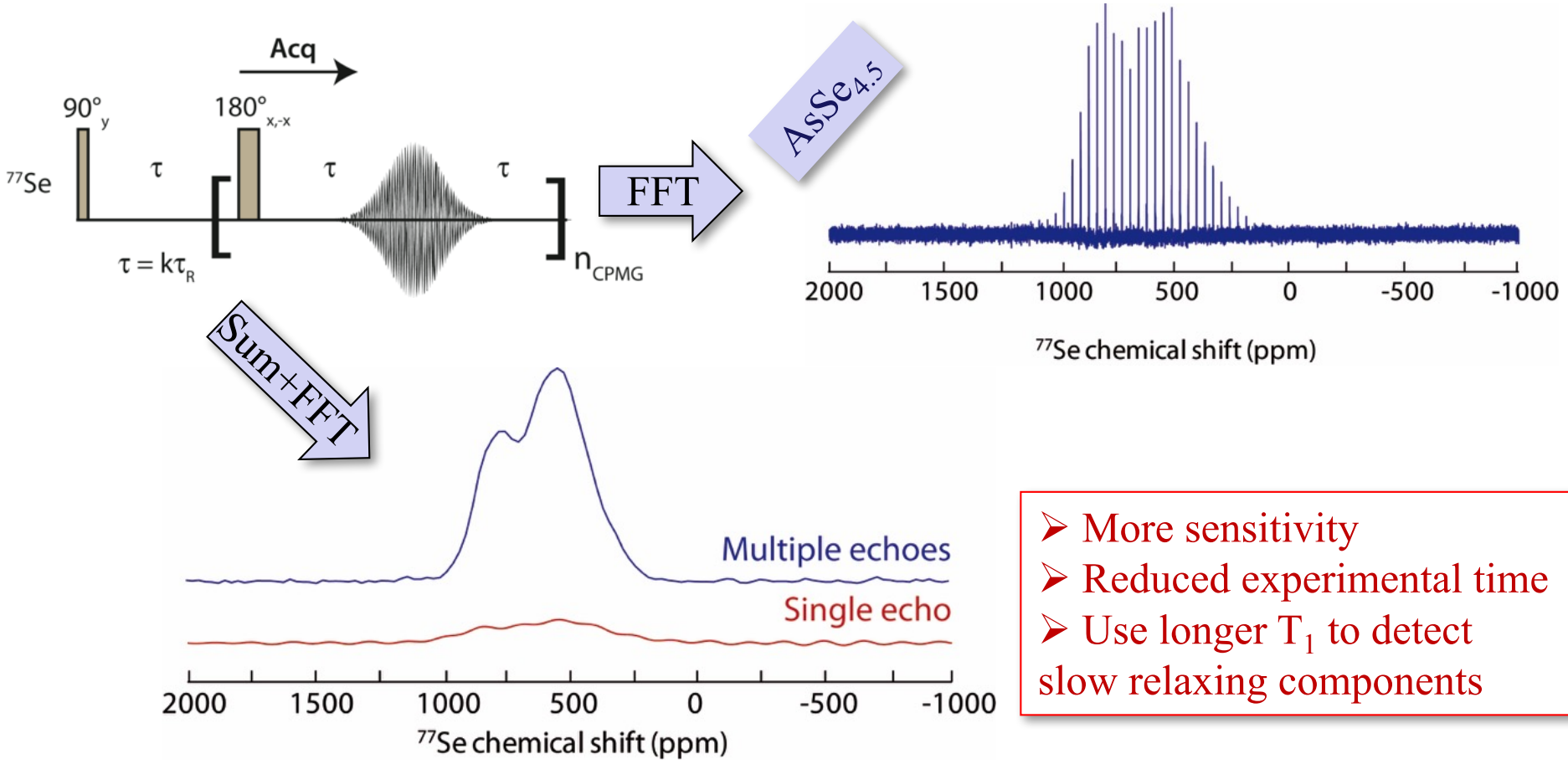


Repeating the spin-echo… until there is no signal left

The Carr-Purcell-Meiboom-Gill CPMG experiment

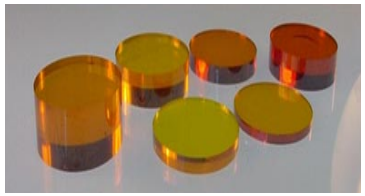
If T_2 permits, repeating the spin-echo (30-200x) experiment improves the sensitivity !

The CPMG sequence can be directly Fourier trans- formed to yield a spikelet spectrum



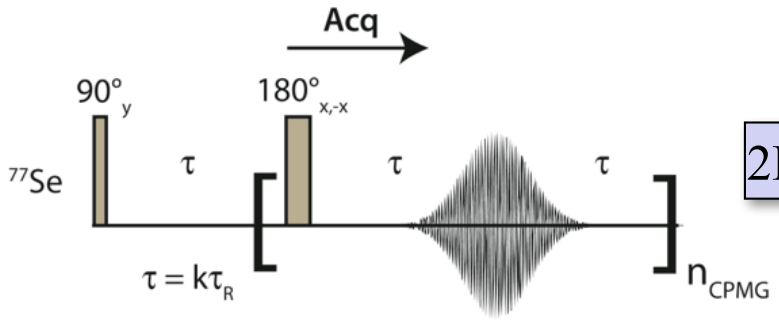
- More sensitivity
- Reduced experimental time
- Use longer T_1 to detect slow relaxing components

M.Deschamps, C.Roiland, B.Bureau, G.Yang, L.Le Pollès, D.Massiot, *Solid State NMR,* 40,2, 72-77(2011)

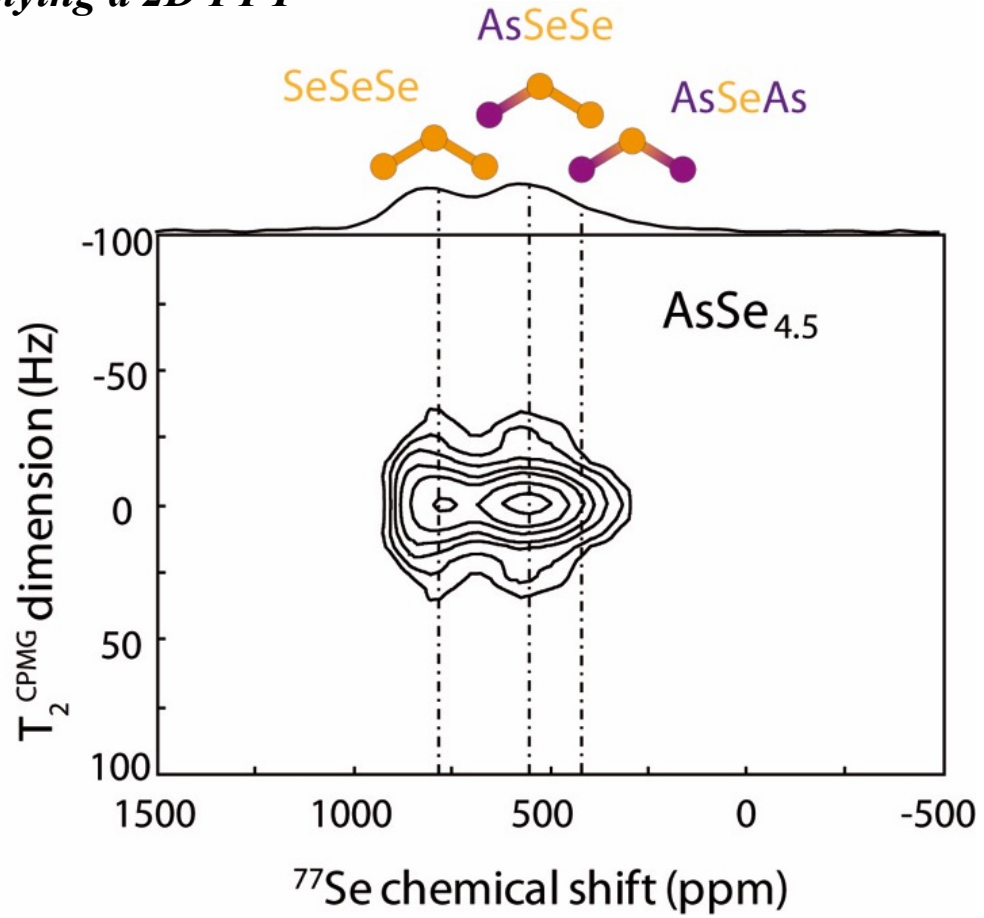


2D CPMG,
using the spins behaviors during the echo train

Create an indirect T2 CPMG dimension,
by aligning the echoes in the time domain before applying a 2D FFT



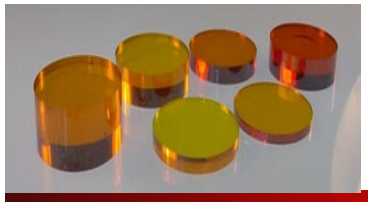
2D FFT



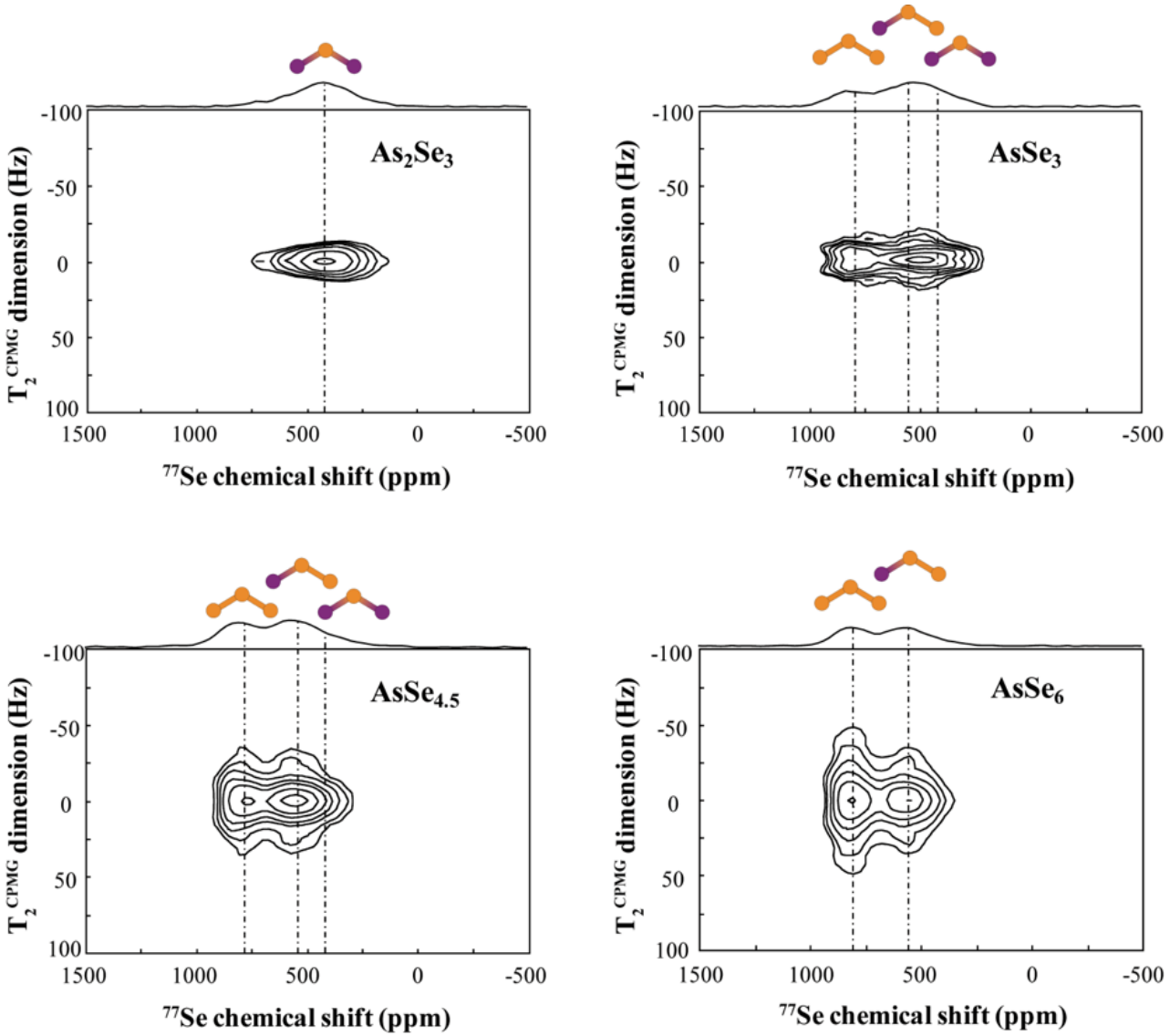
The T2 CPMG indirect dimension give account of the J-couplings

The direct dimension yields a spectrum directly comparable to the spin echo MAS spectrum

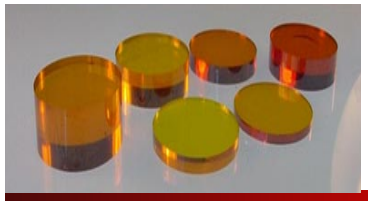
J.W. Wiench, V.S.-Y. Lin, M. Pruski, J. Magn. Reson. 193 (2008) 233–242



2D CPMG: “J-resolved”



- Help at distinguishing three kind of broad line around 800 ppm, 550 ppm, 380 ppm
- The poorer the composition in Se and the weaker the J coupling in the second dimension.

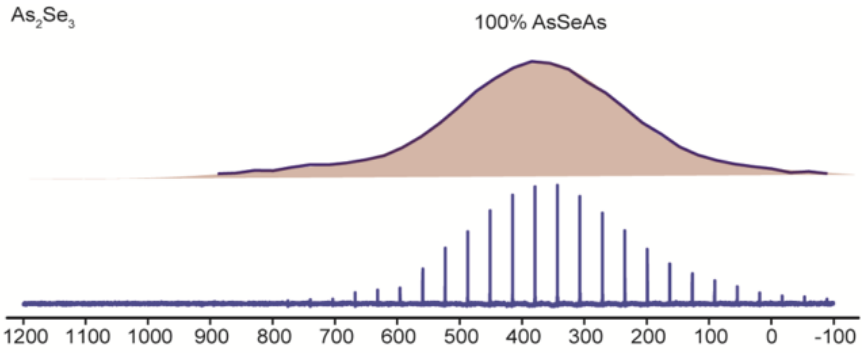


1D CPMG ^{77}Se experiments

7T (low field) , 3.2mm MAS probe (high spinning speed)
→ **Very small spinning sidebands** at 20 kHz MAS
(sidebands every 350 ppm, undetected except for AsSeAs specy)

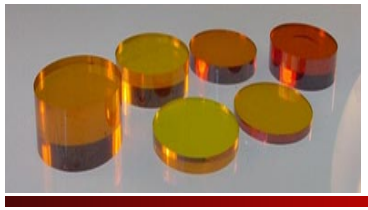
Quantitative spectra:
→ 1day of NMR time with 300s relaxation delay for complete relaxation

Interpretation of ^{77}Se NMR spectra using **MAPLE to fit** several spectra **simultaneously**, using the areas of the CPMG spikelets



As_2Se_3 = 100% AsSeAs Gaussian line with two spinning sidebands (7-8% of the intensity of the main peak)

Same NMR parameters for each species: AsSeAs, AsSeSe and SeSeSe

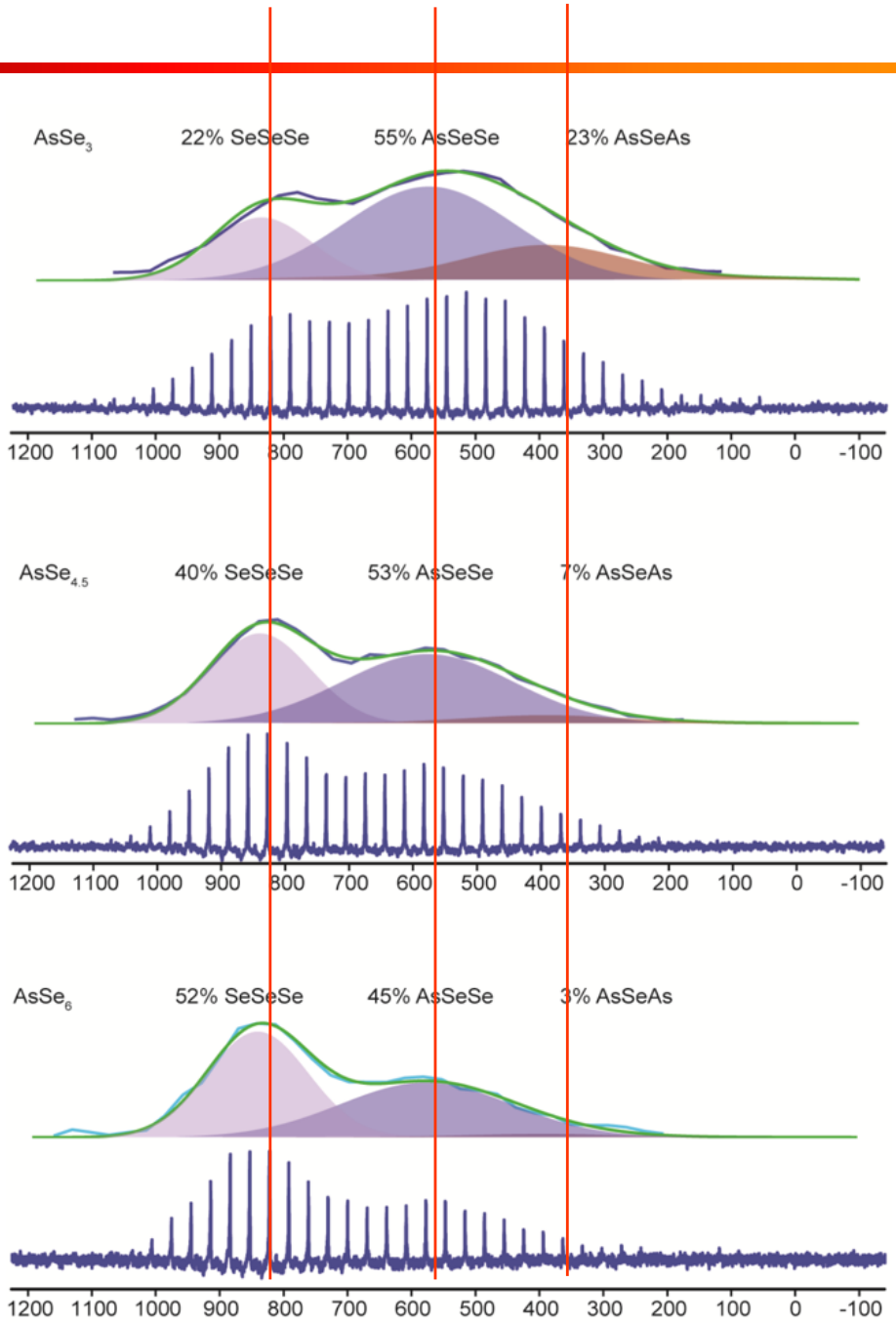


As_2Se_3 CPMG spectrum

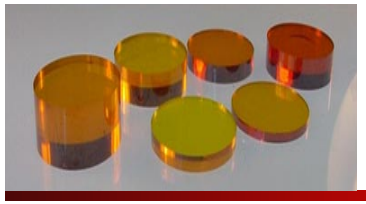
$AsSe_3$

$AsSe_{4.5}$

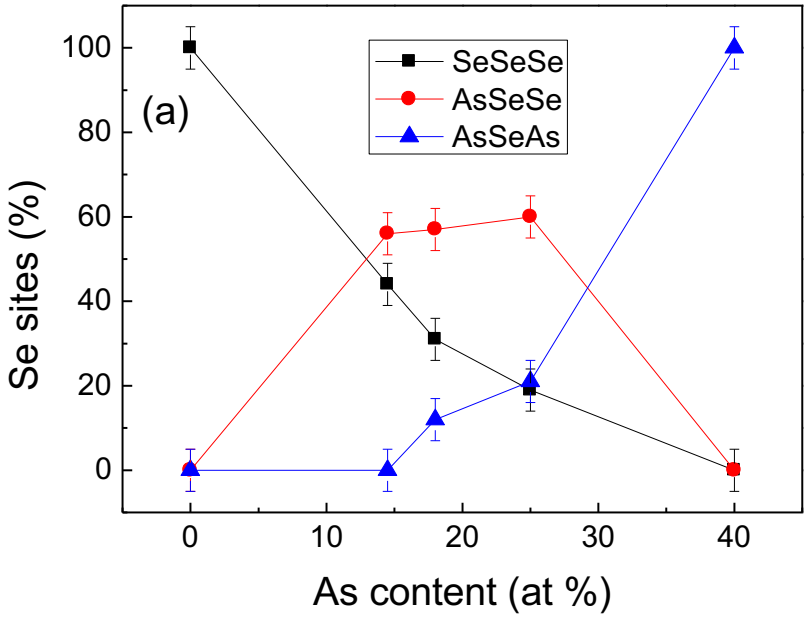
$AsSe_6$



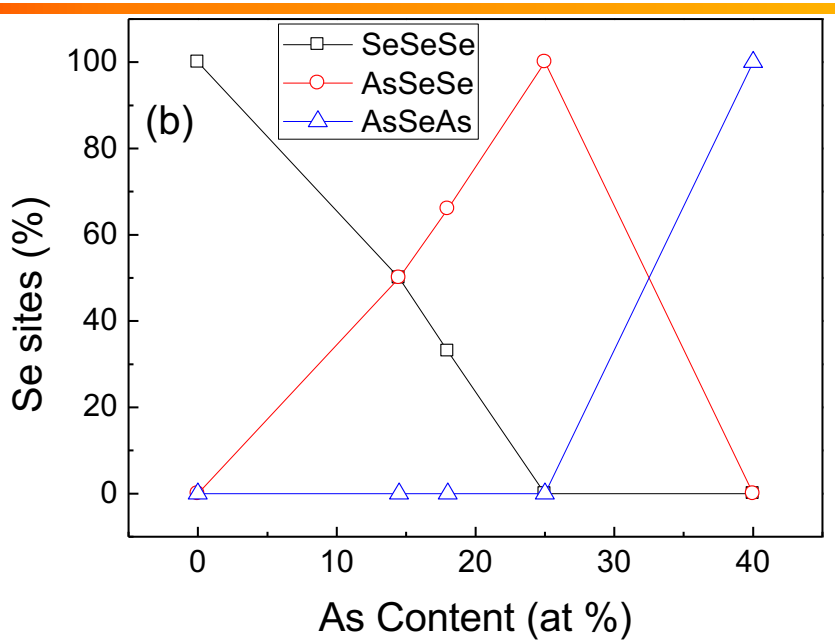
Fitted together with previously fixed parameters for the AsSeAs line



^{77}Se solid state NMR 1D



Integrated intensities of the three Se sites from the reconstruction of NMR spectra



The integrated intensities expected with the CCM

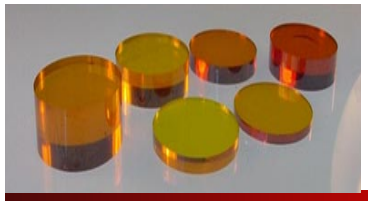
for $AsSe_3$, and other Se-rich glasses, this equilibrium has to considered:

$$2\ AsSeSeAs \leftrightarrow AsSeAs + AsSeSeSeAs$$

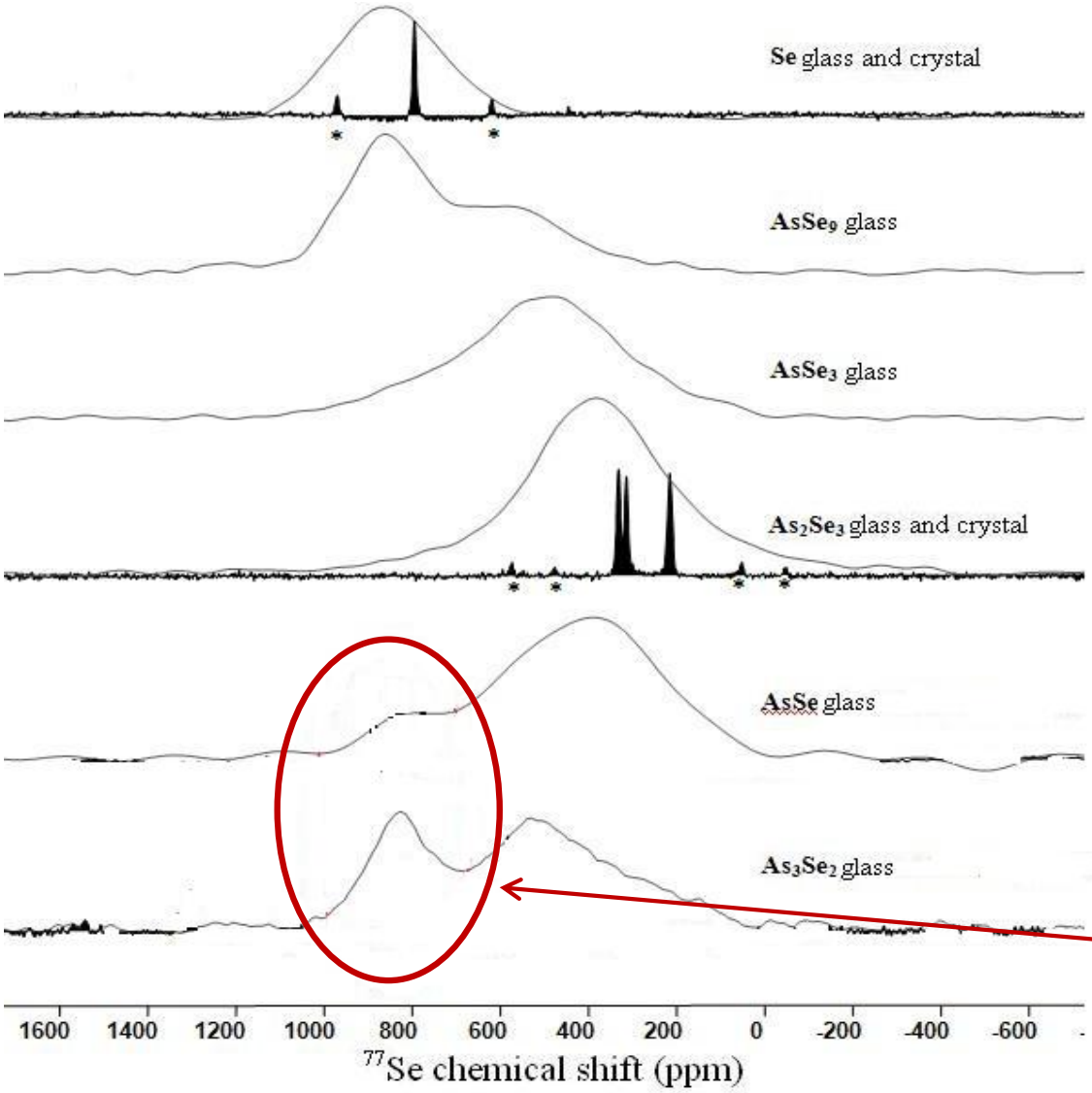
This chain length distribution explains the discrepancy with the basic CCM
that was not pointed out by the data previously published

Nevertheless, 1D/2D NMR spectra reveals that the network reticulation increases,
which is in full agreement with the measured physical properties.

B. Bureau, J. Troles, M. Le Floch, F. Smektala, G. Silly, J. Lucas, Solid State Sci. 5 (2003) 219–224
M.Deschamps, C.Roiland, B.Bureau, G.Yang, L.Le Pollès, D.Massiot, Solid State NMR, 40,2, 72-77(2011)



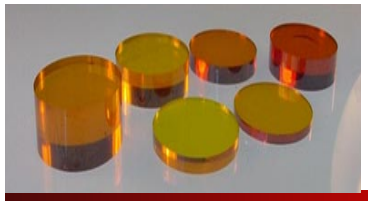
^{77}Se solid state NMR for x>0.4



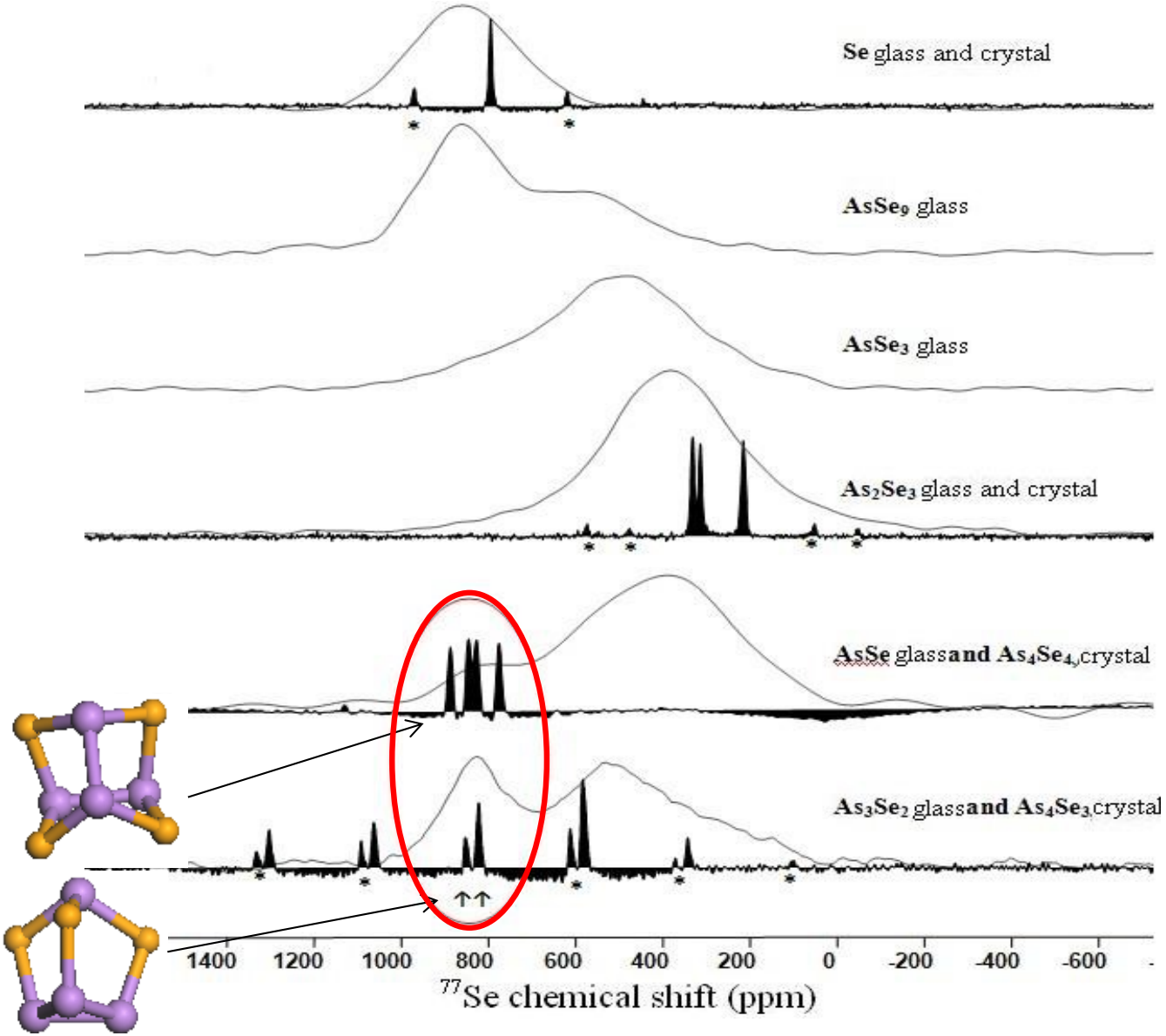
^{77}Se NMR spectra for whole As_xSe_{1-x} glassy system at room temperature

new spectra for As-rich glasses.

new lines, not expected at all at such chemical shift values !



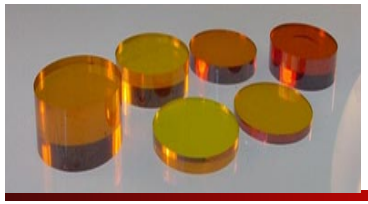
^{77}Se solid state NMR 1D



^{77}Se NMR spectra for whole As_xSe_{1-x} glassy system and crystals As_4Se_4 and As_4Se_3 at room temperature

The new lines have to be attributed to As_4Se_4 and As_4Se_3 cages

G Yang, B Bureau, et al. Phys Rev B 82, 19 195206, pp8 (2010)



^{77}Se chemical shift calculation

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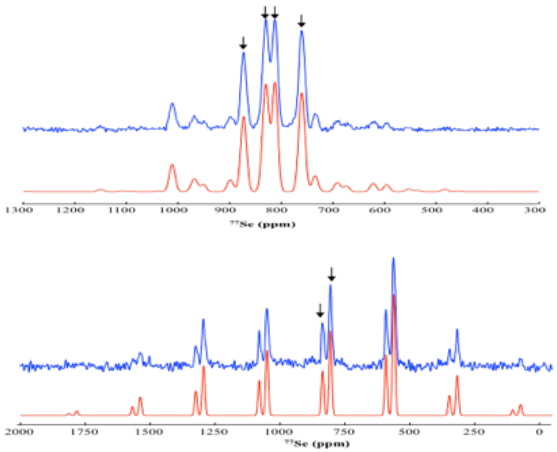
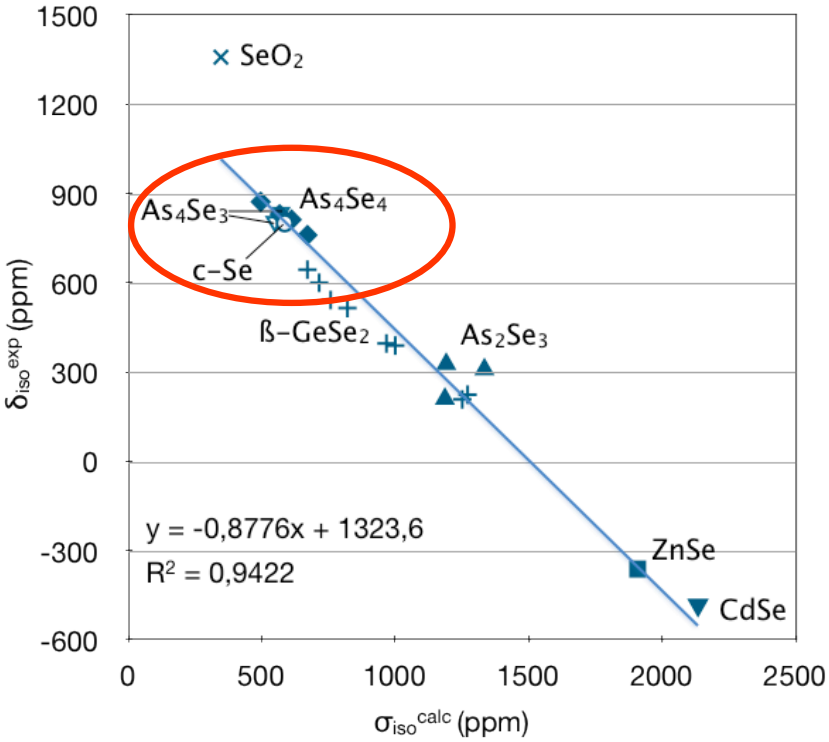
As_4Se_4

As_4Se_3

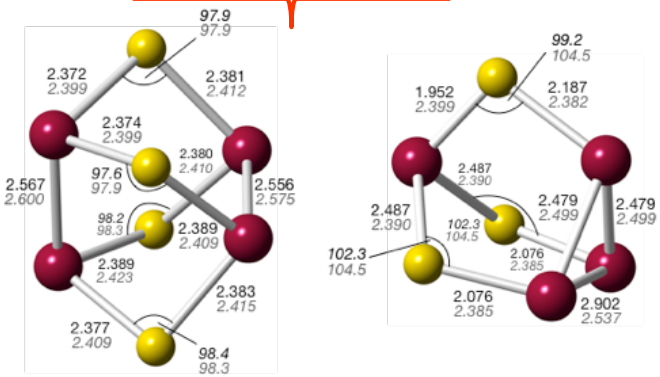




Chemical shift were calculated from the structural data with CASTEP* using the GIPAW methods

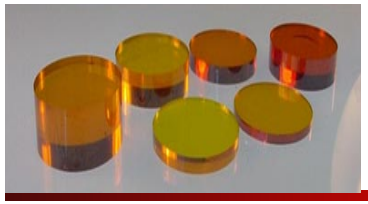
Experimental and calculated data are in good agreement

Confirm that As_4Se_4 and As_4Se_3 molecules give rise to NMR signal around 800 ppm, close to pure-Se

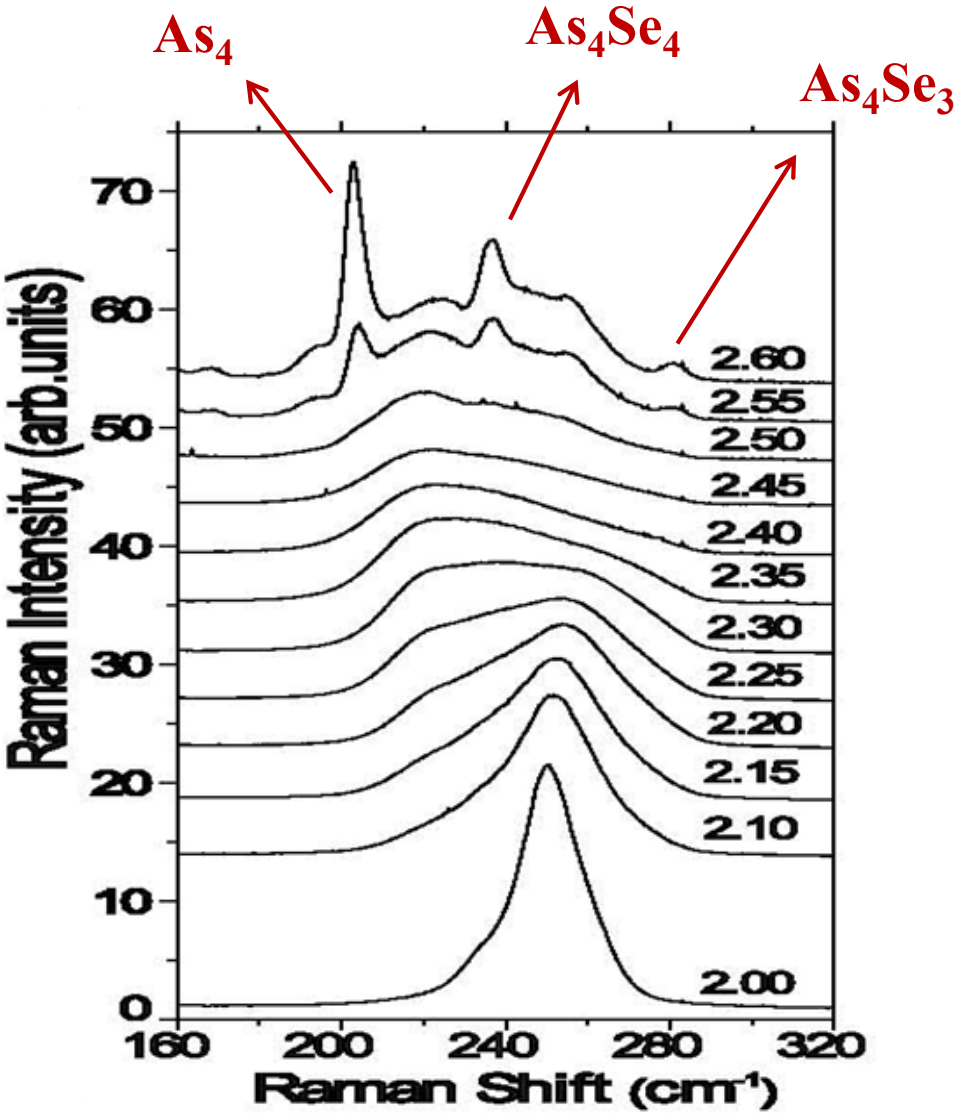


*S. J. Clark, M. D. Segall, C. J. Pickard, et al., *Zeitschrift für Kristallographie* 2005, *220*, 567–570.

K. Sykina, G. Yang, L. Le Pollès, E. Le Fur, C. Roiland, C. Pickard, B. Bureau, E Furet PCCP 2013



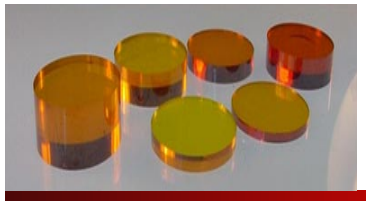
Raman spectra



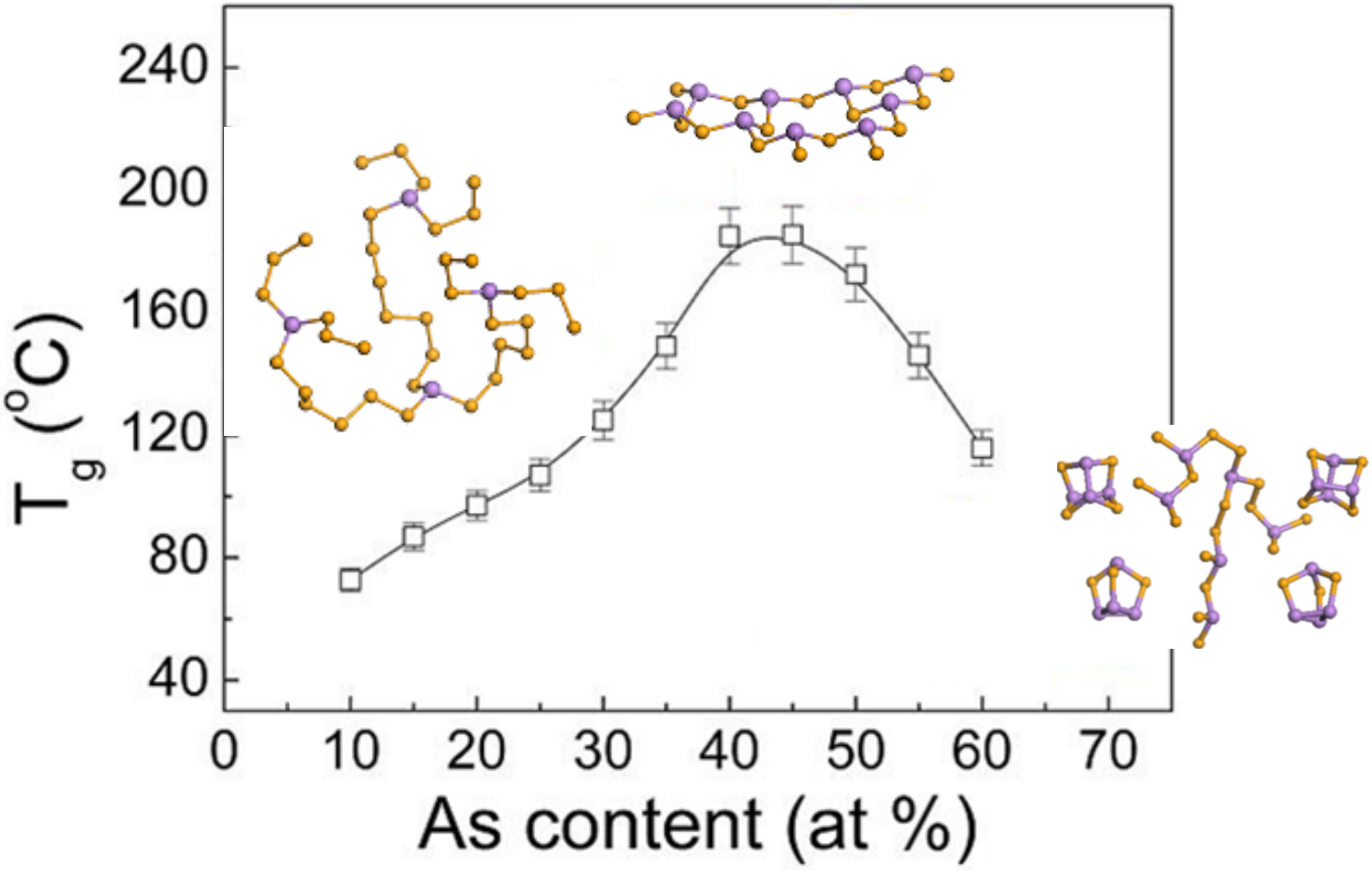
Raman spectra for As_xSe_{1-x} glassy system at room temperature

Confirms the existence of the cages in the As-rich glass structures

Also shown the existence of As_4 molecules

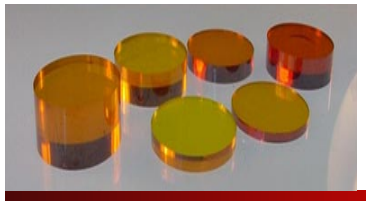


Conclusions on As_xSe_{1-x}



In the Se-rich region : evolution from a 1-D chain structure to a 2-D pyramidal network following (more or less) the CCM

transitions to a lower dimension structure composed of a pyramidal backbone mixing with an increasing number of 0D molecular inclusions



recent refinement on the As_xSe_{1-x}

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

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Structure of Arsenic Selenide Glasses Studied by NMR: Selenium Chain Length Distributions and the Flory Model

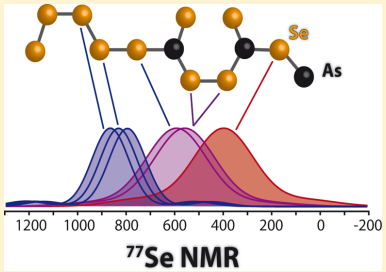
Michaël Deschamps,*,† Cécile Genevois,† Shuo Cui,‡ Claire Roiland,‡ Laurent LePollès,‡ Eric Furet,‡ Dominique Massiot,† and Bruno Bureau‡

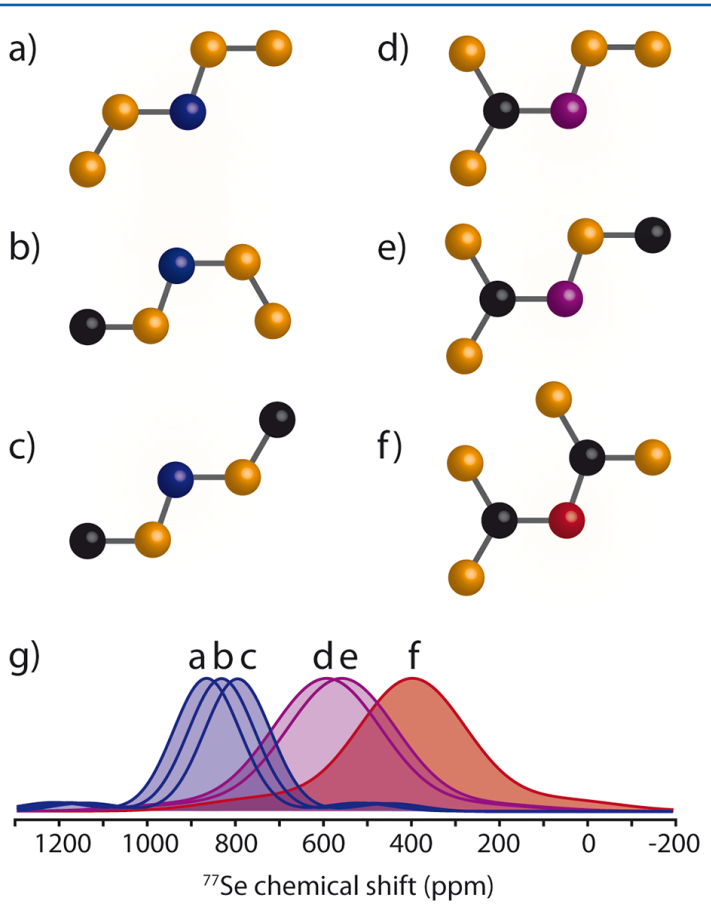
†CNRS, CEMHTI UPR3079, Univ. Orléans, F-45071 Orléans, France

‡Institut des Sciences Chimiques de Rennes, UMR-CNRS 6226, Université de Rennes 1, 35042 Rennes cedex, France

Supporting Information

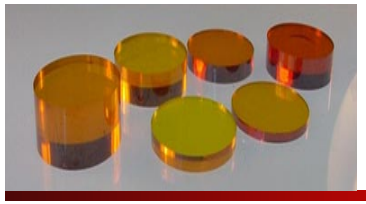
ABSTRACT: Five homogeneous arsenic selenide glasses with target compositions As_2Se_3, $AsSe_2$, $AsSe_3$, $AsSe_{4.5}$, and $AsSe_6$ were studied quantitatively by ^{77}Se Carr−Purcell−Meiboom−Gill magic-angle spinning NMR and transmission electron microscopy−energy-dispersive X-ray spectroscopy. The entire set of NMR spectra is simultaneously fitted with six distinct environments taking into account the effect of first and second neighbors on the position of the ^{77}Se resonance. The selenium chains are bound at each end to trivalent arsenic atoms, and the chain length distribution can be modeled with the Flory theory, which is well-known in polymer science and is used here for the first time to model the probability of finding each selenium environment in a selenide glass. No arsenic homopolar bond is detected in our experiments.



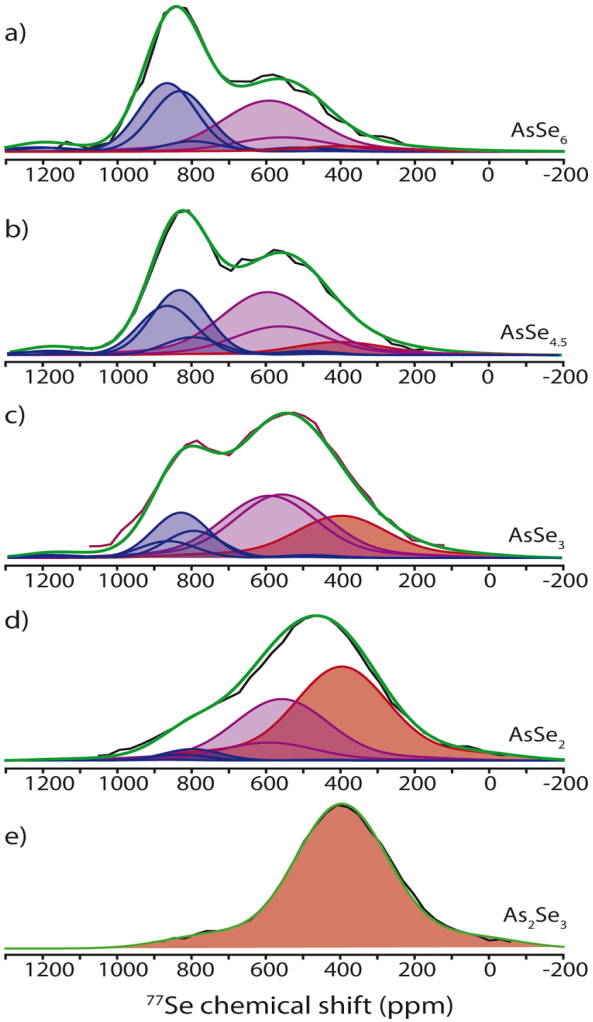


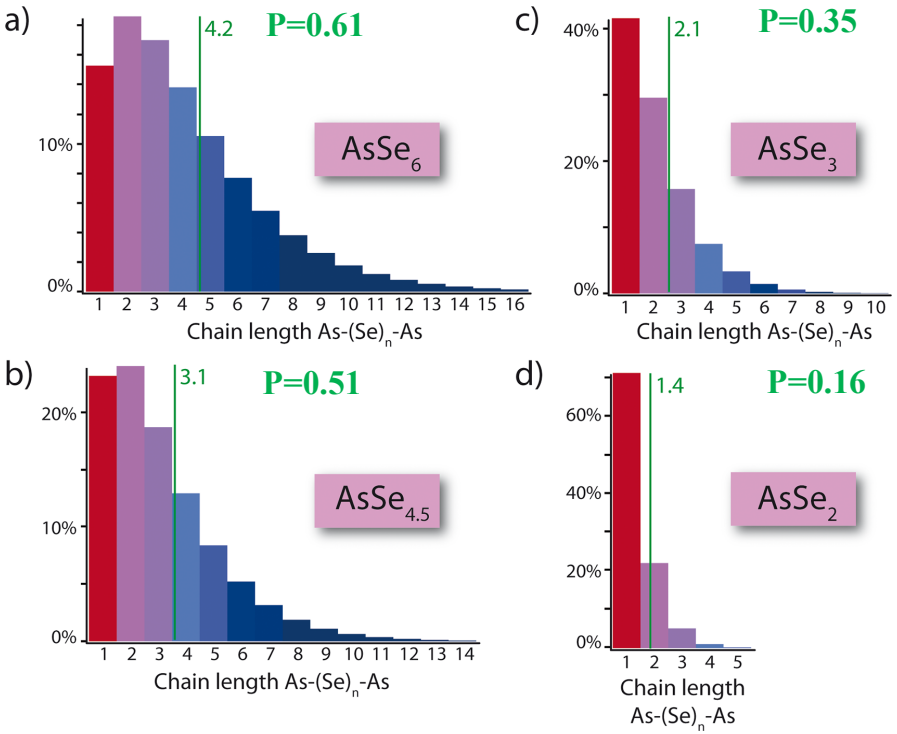
- **Taking a special care to the relaxation time (300s)**
- **Also considering the spinning side bands for the reconstruction**
- **Taking into account Se second neighboors for the reconstruction**
- **Using Flory model* to give account of the chain lengths between reticulation**

*The probabilities, P(n), of finding a chain of length n was set to $P(n)= np^{n-1}(1-p)^2$ where p is a fitting parameter, and the proportions of each environment (a to f) were calculated accordingly



recent refinement on the As_xSe_{1-x}

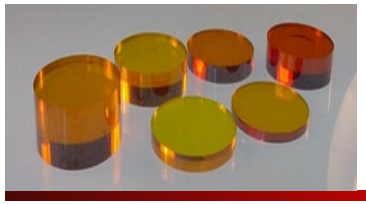




According to the Flory model, the average chain length is $\boldsymbol{n = \frac{1+p}{1-p}}$

p being the probablity for a monomer to connect an other monomer

The Flory model can be applied to arsenic selenide to retrieve information on the distribution of chain length,
The Flory theory was originally introduced to describe polymers



Looks like former work on Te_xSe_{1-x}

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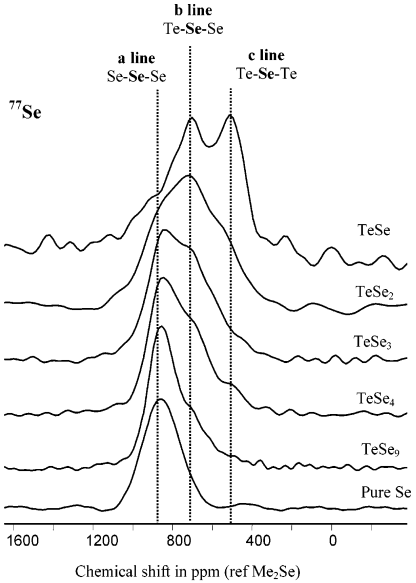
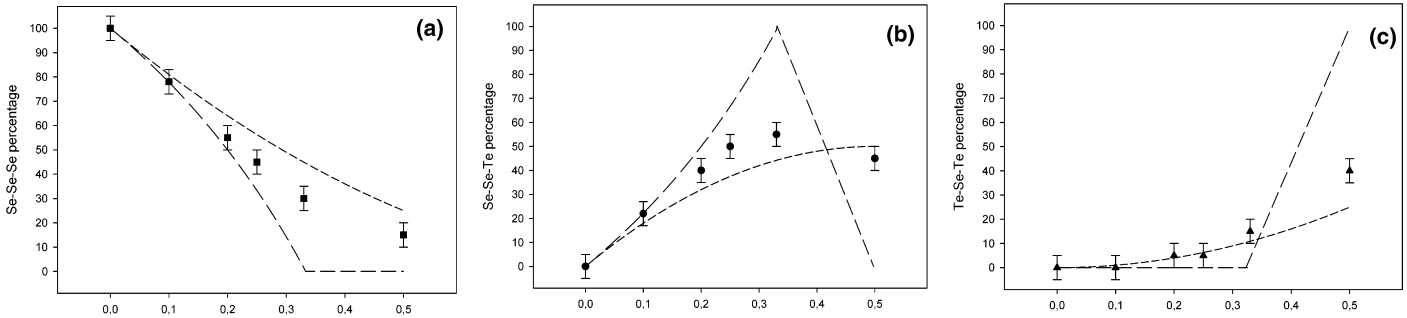
6130 *J. Phys. Chem. B* **2005,** *109,* 6130−6135

Selenium−Tellurium Sequences in Binary Glasses as Depicted by ^{77}Se and ^{125}Te NMR

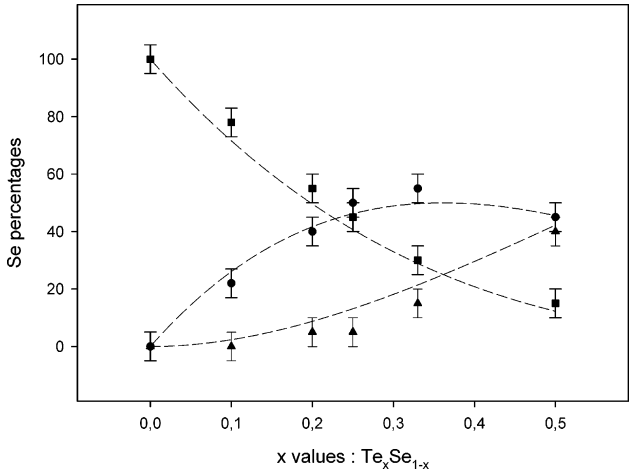
Bruno Bureau,* Catherine Boussard-Plédel, Marie LeFloch, Johann Troles, Frédéric Smektala, and Jacques Lucas





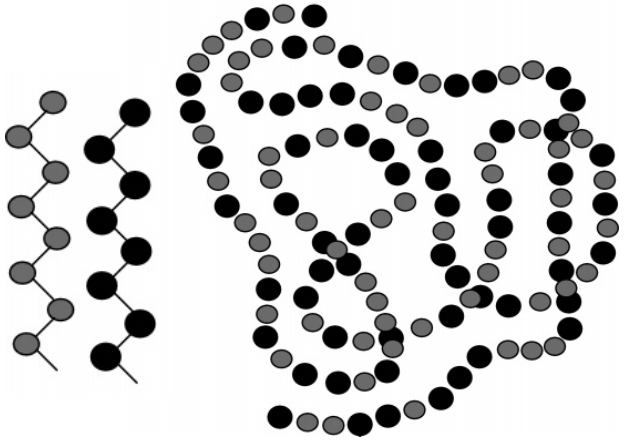
CCM, **heteropolar bonds are strongly priviledged**
Random distribution, **P(x)=x**

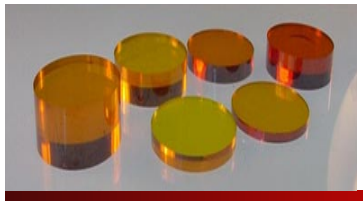
- A compromise has to be found between an ideal dilution and a random distribution of Te and Se atoms.
- The probability to meet Te connected to Se is then given by $P_k(x)=\frac{0.5-k}{0.25}.x^2+\frac{k-0.25}{0.25}.x$



With k=0.65

Heteropolar bonds priviledged





Chemometric methods applied to solid state NMR ?

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Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

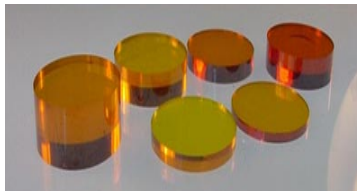
journal homepage: www.elsevier.com/locate/jnoncrysol

Structure of arsenic selenide glasses by Raman and ^{77}Se NMR with a multivariate curve resolution approach

Zdeněk Černošek [a], Michaël Deschamps [b], Virginie Nazabal [c], Claudia Goncalvez [c], Claire Roiland [c], Jana Holubová [a], Eva Černošková [d], Catherine Boussard [c], Bruno Bureau [c,*]

- Multivariate resolution

- 2D correlation maps



multivariate curve resolution

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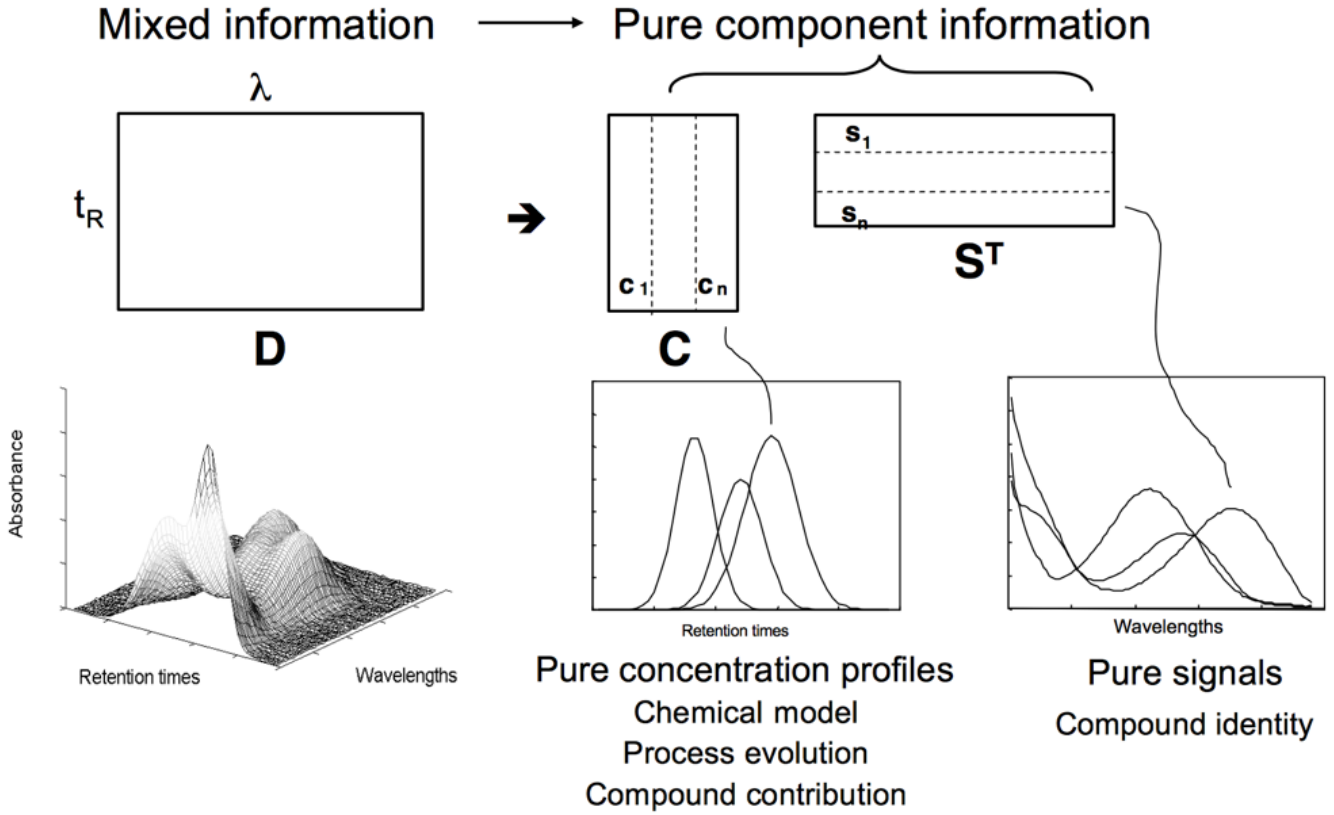
Group of techniques which help resolve mixtures by determining the number of constituents, their response profiles (spectra, pH profiles, time profiles, elution profiles) and their estimated concentrations, when no prior information is available about the nature and composition of these mixtures.

Keywords: Partial Least Square (PLS) regression, Principle Component Analysis …



Journal of Chemometrics, 1995, 9, 31-58; Chemomet.Intel. Lab. Systems, 1995, 30, 133-146
Journal of Chemometrics, 2001, 15, 749-7; Analytica Chimica Acta, 2003, 500,195-210

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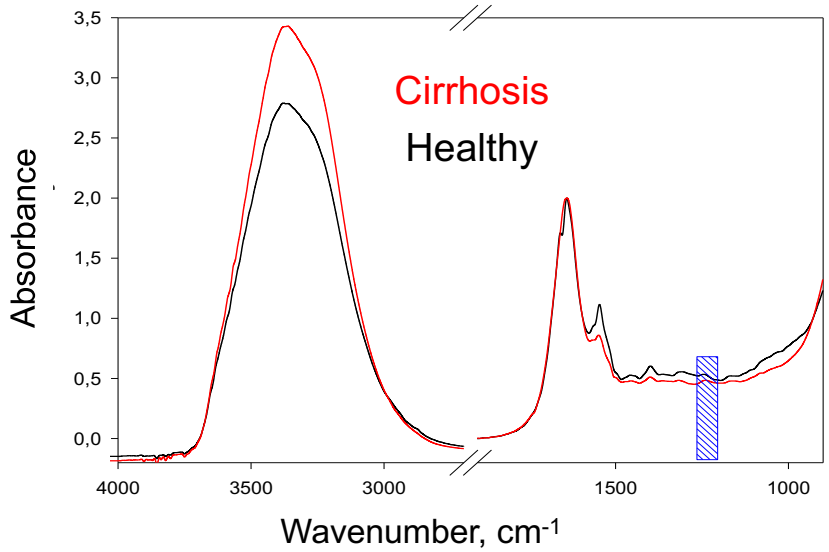
Alcoholic cirrhosis

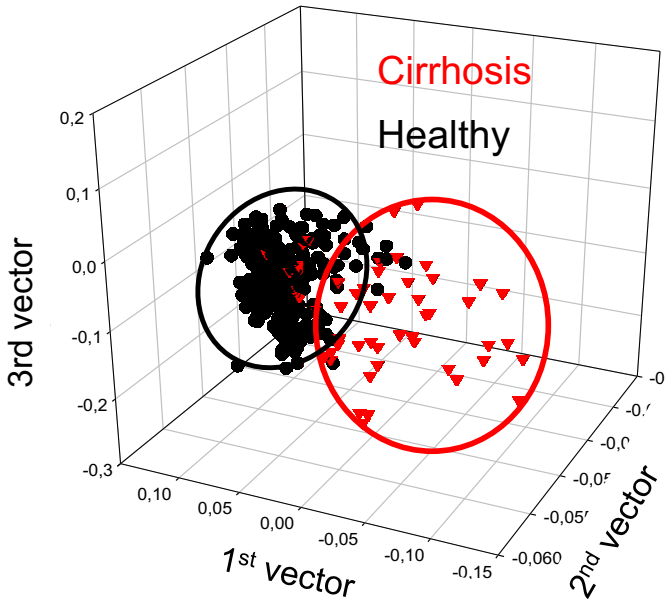
From clinical & histologic data

↳ Decrease in the percentage of proteins

Average spectrum



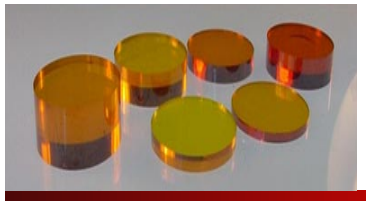
PCA map



Studied region spectra : 1257-1308 cm^{-1}

↳ Area of proteins (Amide III)

➡ **Separation of the 2 metabolic states (with a small overlap)**



What about MCR applied to solid state NMR ?

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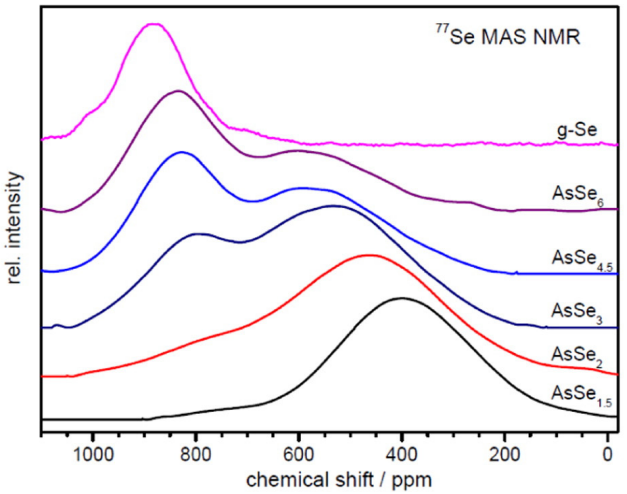
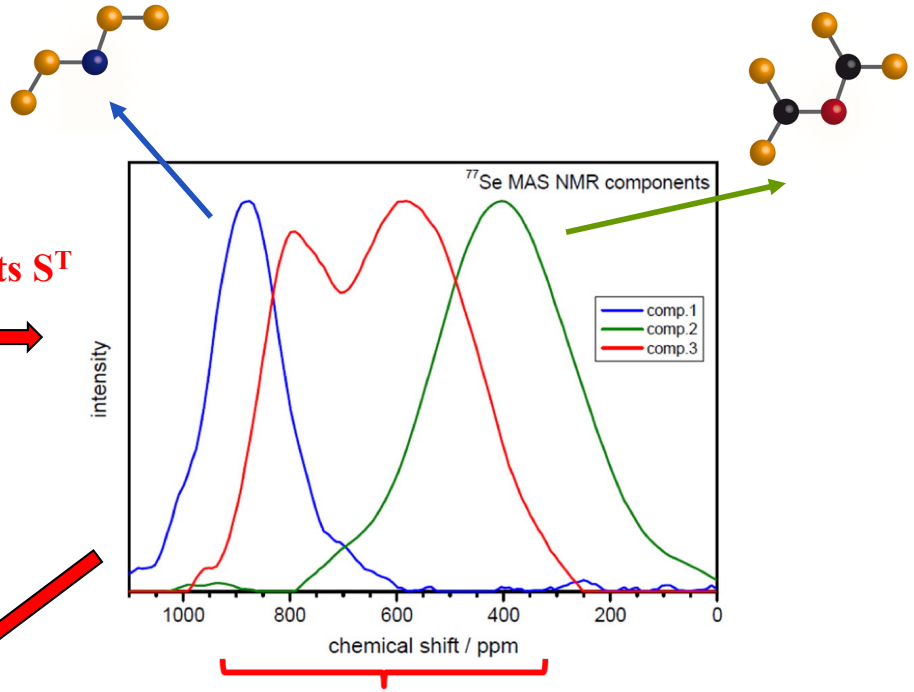
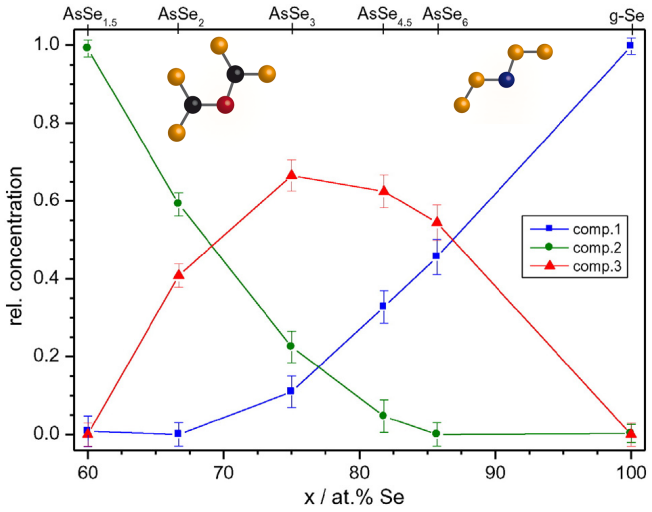
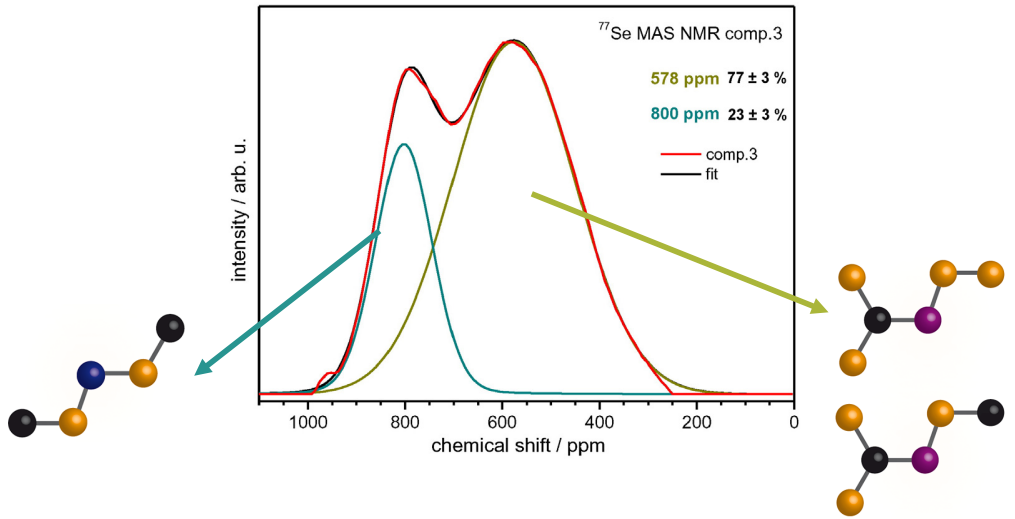


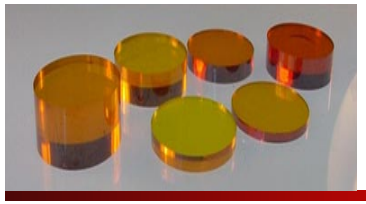
3 principle components S^T



With their intensities







Correlation maps coupling solid state NMR with Raman

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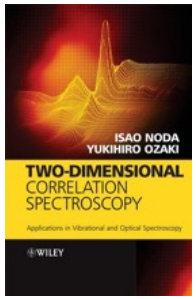
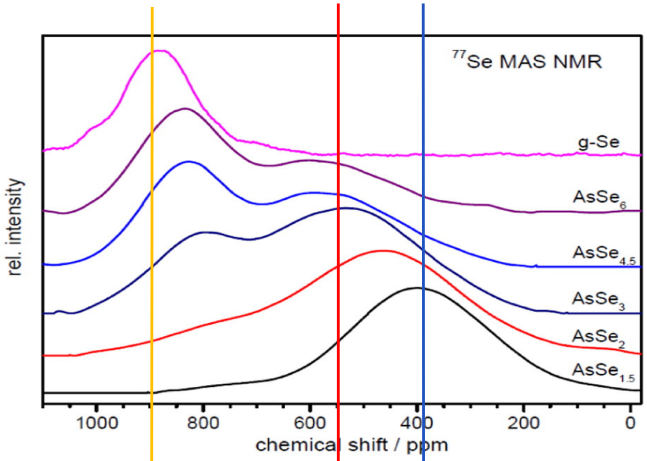
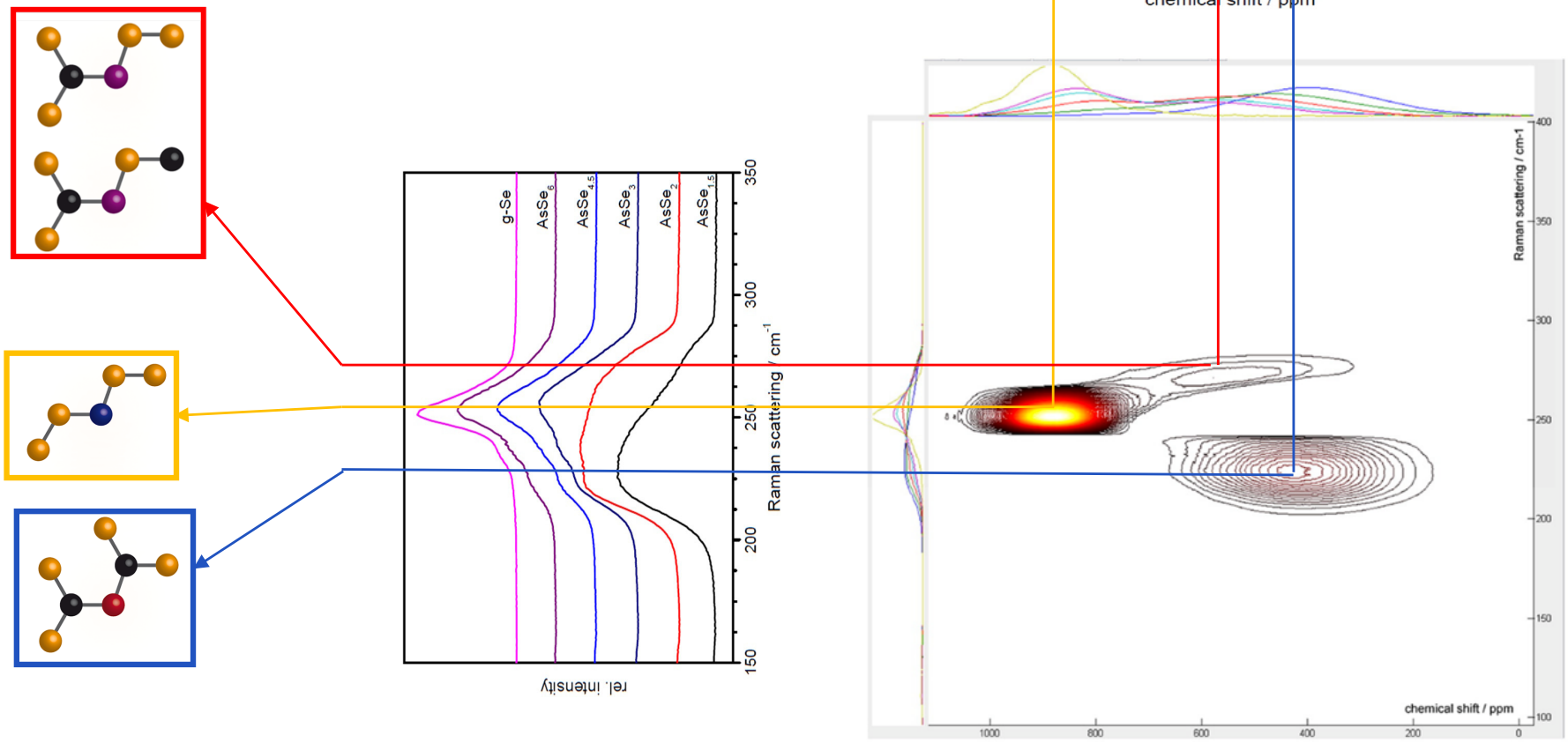
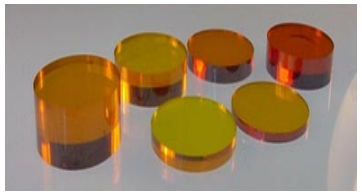


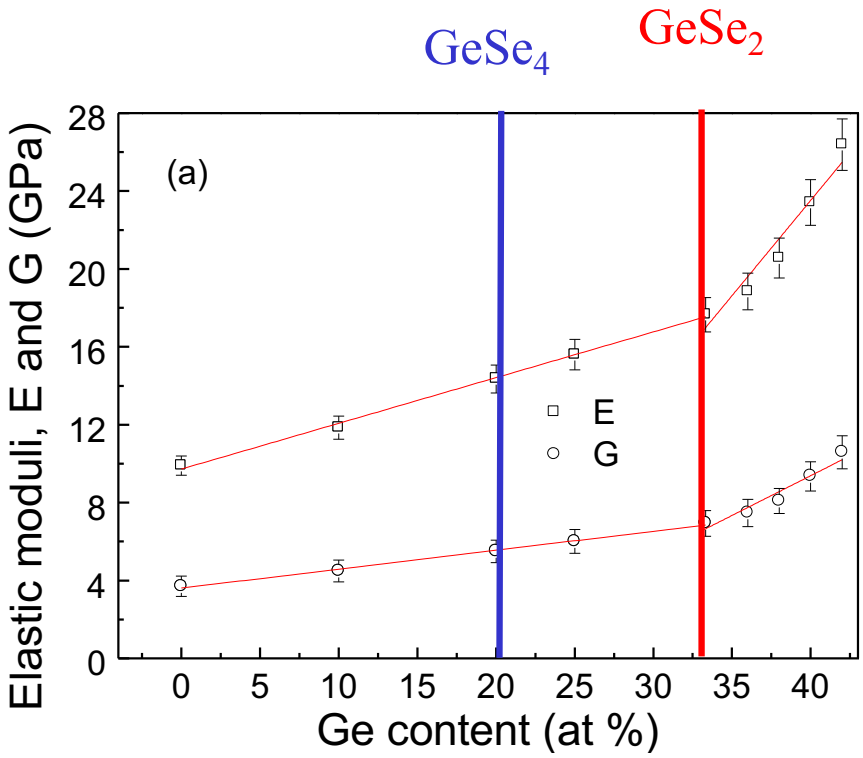
2D Correlation maps enable to identify correlations between two distinct sets of data

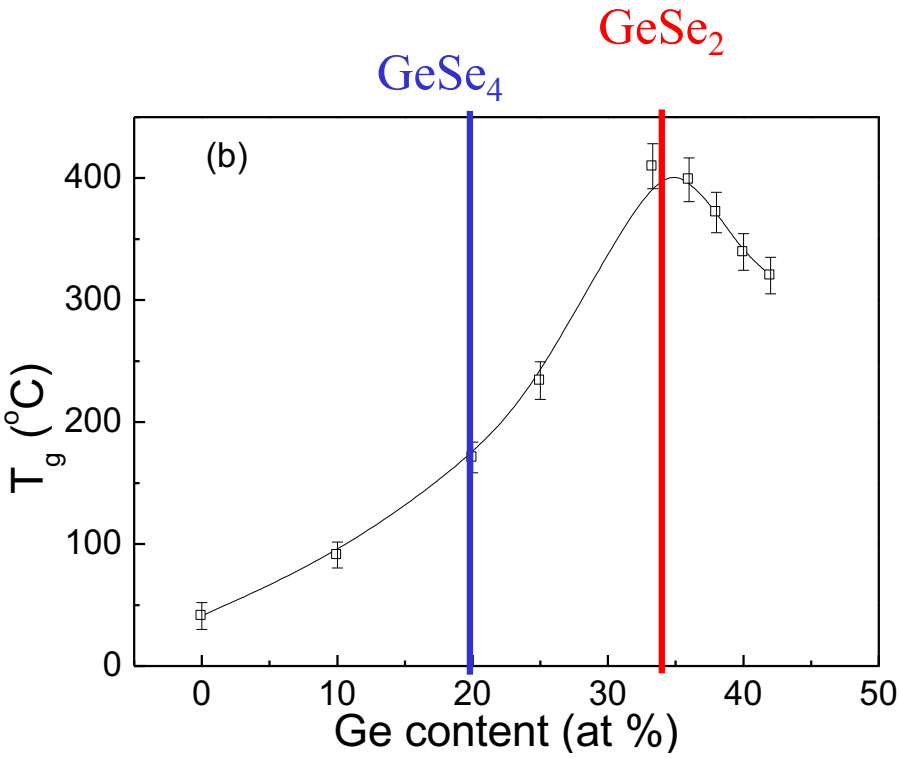






The Ge_xSe_{1-x} binary system

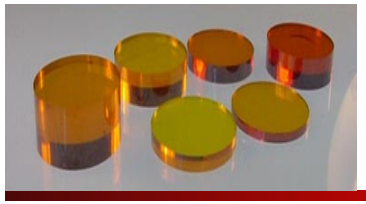




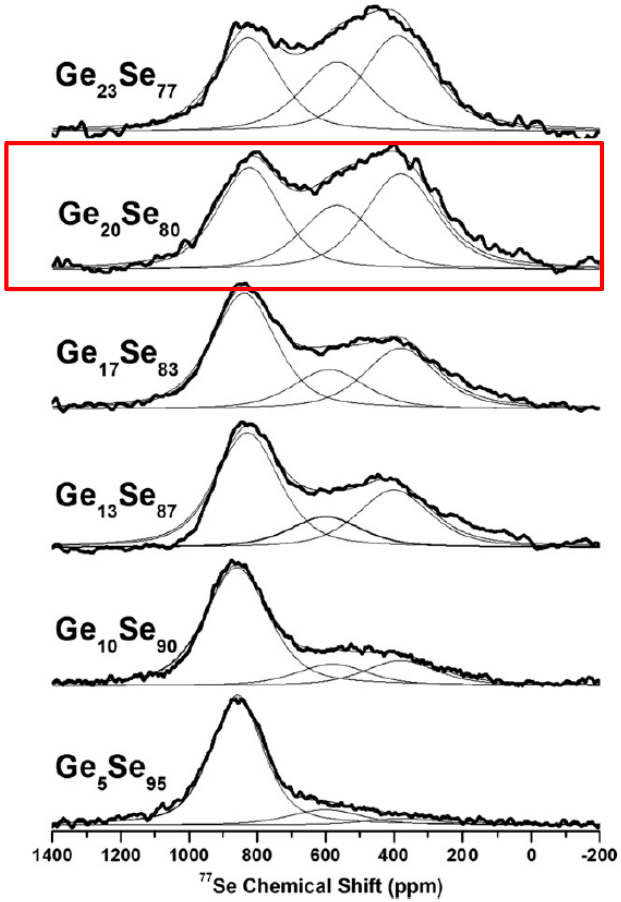
a **breaking point appears**, corresponding to **$GeSe_2$** composition (r=2,67)

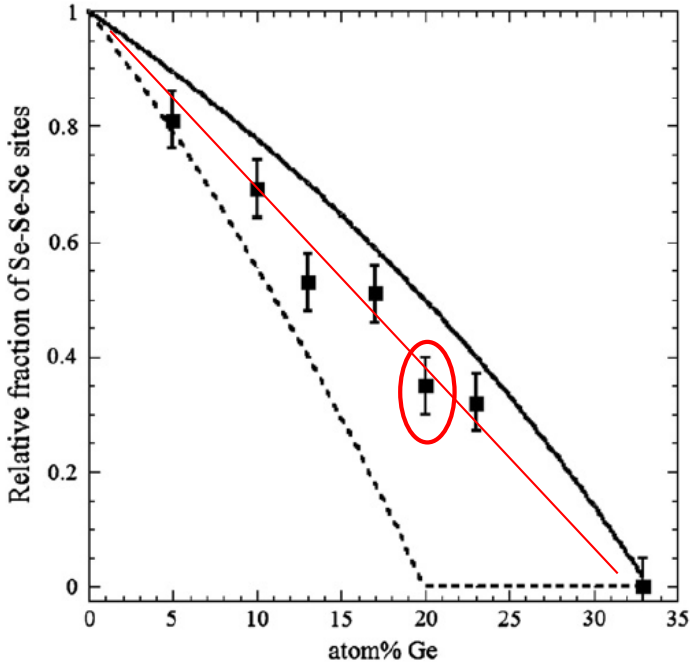
The physical properties vary perfectly **linearly around $GeSe_4$** (r=2,4)

The physical changes have probably to be correlated to the presence of direct Ge-Ge homopolar bonds



^{77}Se NMR on the Ge_xSe_{1-x} system





-The integrated intensities evolution is monotonous from Se (r=2) to Ge_2Se_3 (r=2.8)
-The structural network is intermediate between the CCM and the Clustering Model
-No special structural feature is visible for $GeSe_4$ (average coordination number r = 2.4)

B. Bureau, J. Troles, M. Le Floch, F. Smektala, J. *Lucas, J. of Non-Cryst. Solids, 326*-327 (2003) 58
T. G. Edwards, S. Sen, E.L. Gjersing, J. of Non-Cryst. Solids, 358, 3, 1 (2012) 609-614

Let's go further to the $GeSe_4$ description

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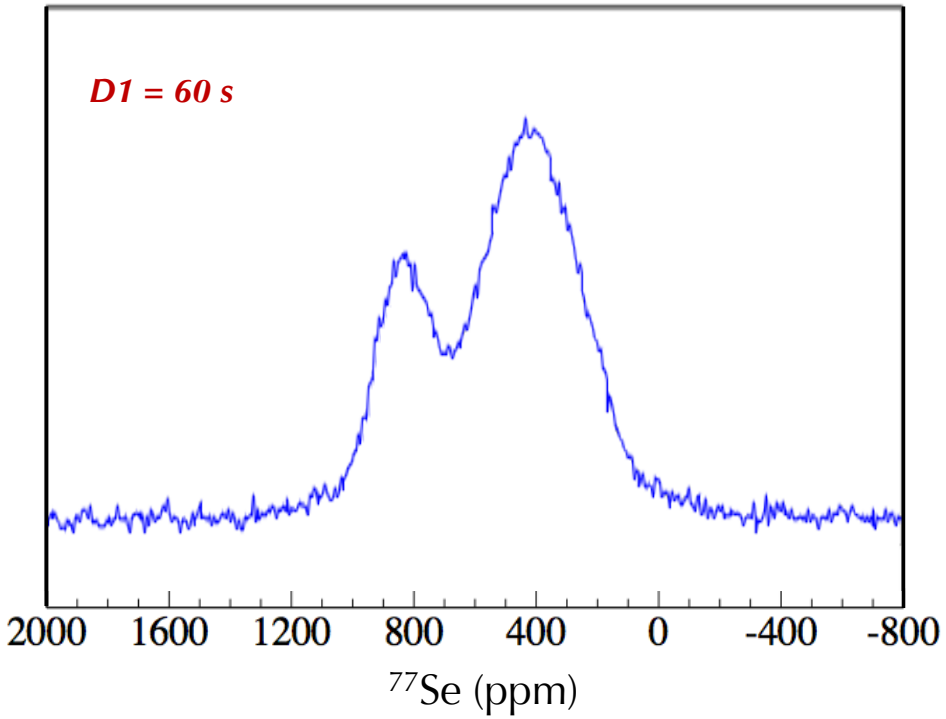
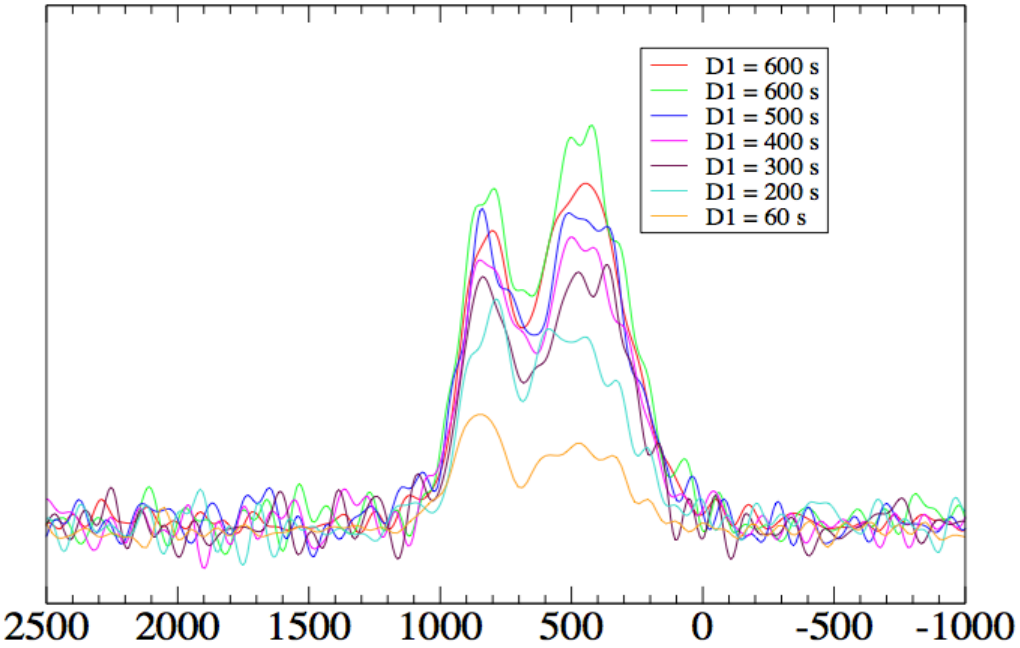
^{77}Se enriched sample (100%)



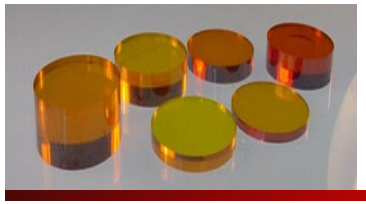
Natural abundance (~7%)



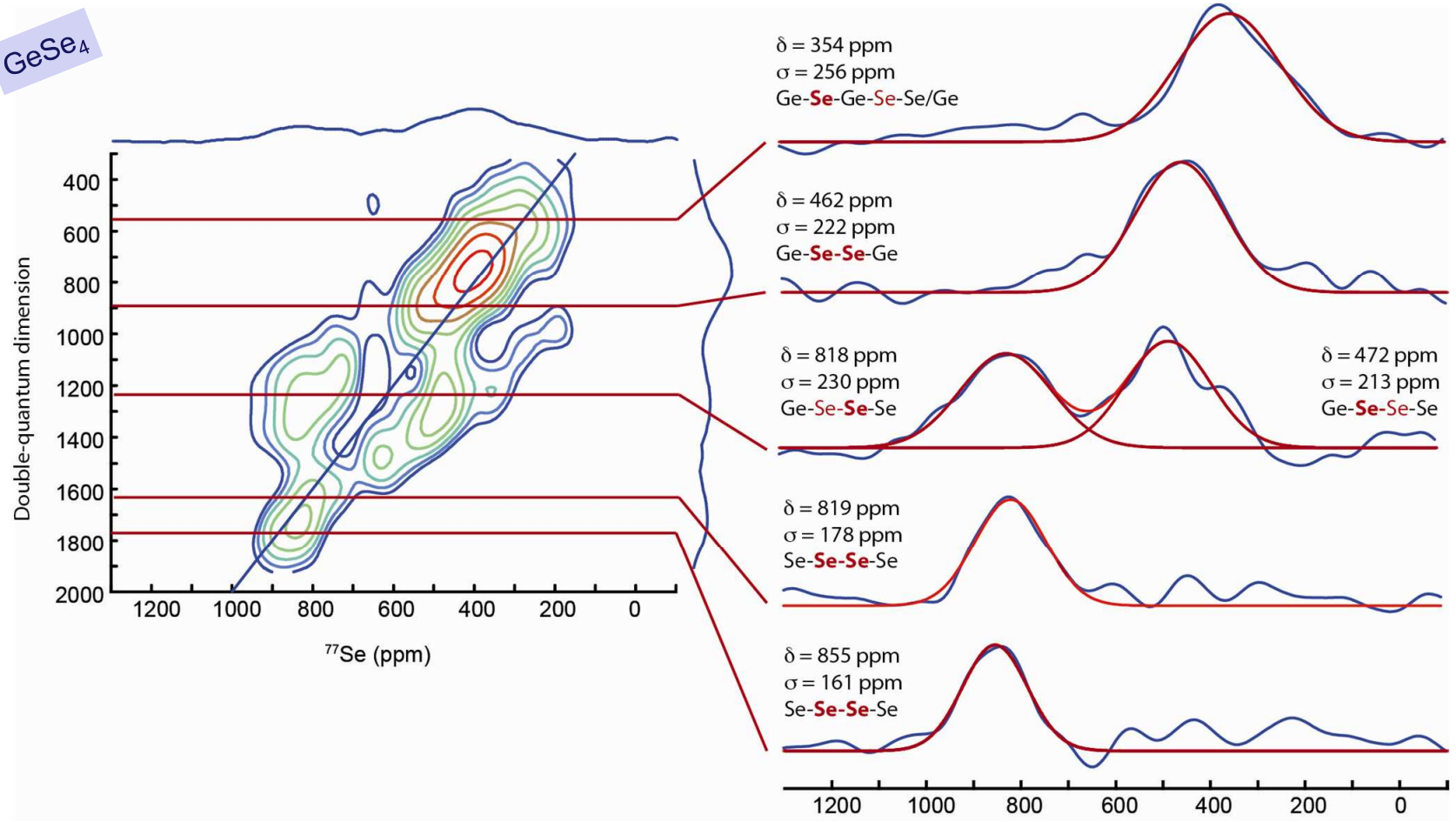
The same lineshape, the peak associated to the Se chains is lower.
60 s were required to stabilize the signal.
the magnetization transfer is greatly improved due to the high concentration of NMR-active isotope

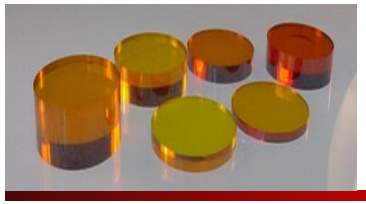
A series of acquisitions performed: D1 from 60 s to 1200 s.
The signal is stabilized for recycle delays higher to 600 s.

→ pays attention to the recycle time D1 to get quantitative spectra



2D correlation spectrum $GeSe_4$





The $GeSe_4$ description

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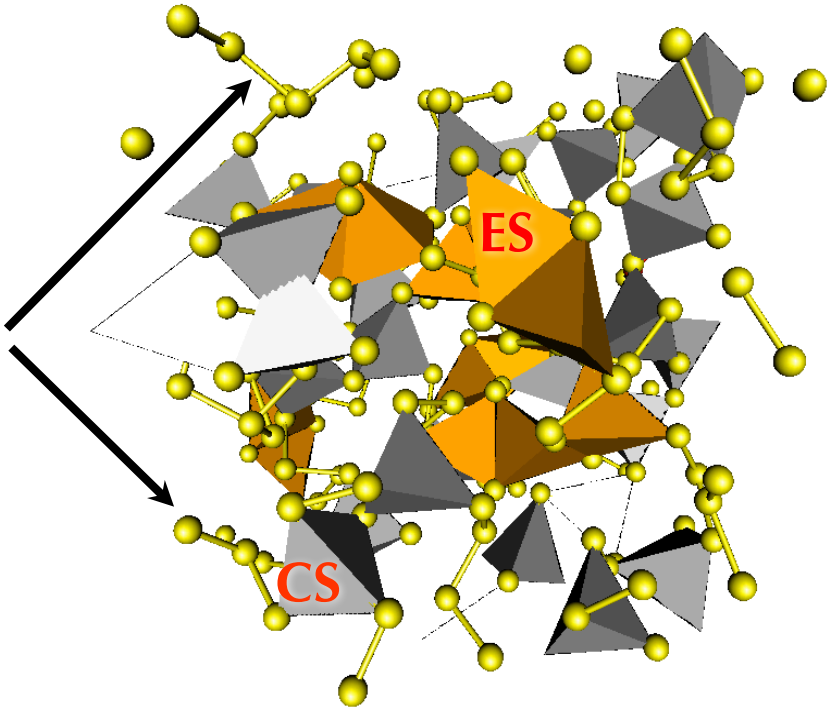
Contents lists available at SciVerse ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Network connectivity and extended Se chains in the atomic structure of glassy $GeSe_4$

Kateryna Sykina [a], Eric Furet [a,*], Bruno Bureau [a], Sébastien Le Roux [b], Carlo Massobrio [b]

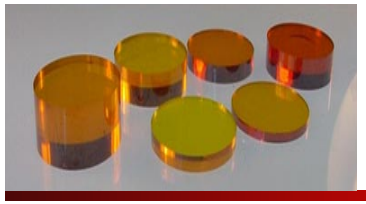


Car-Parrinello molecular dynamics simulations performed using the PBE functional, on a cubic simulation cell of 18.3 $Å^3$ containing 215 **randomly distributed atoms** *

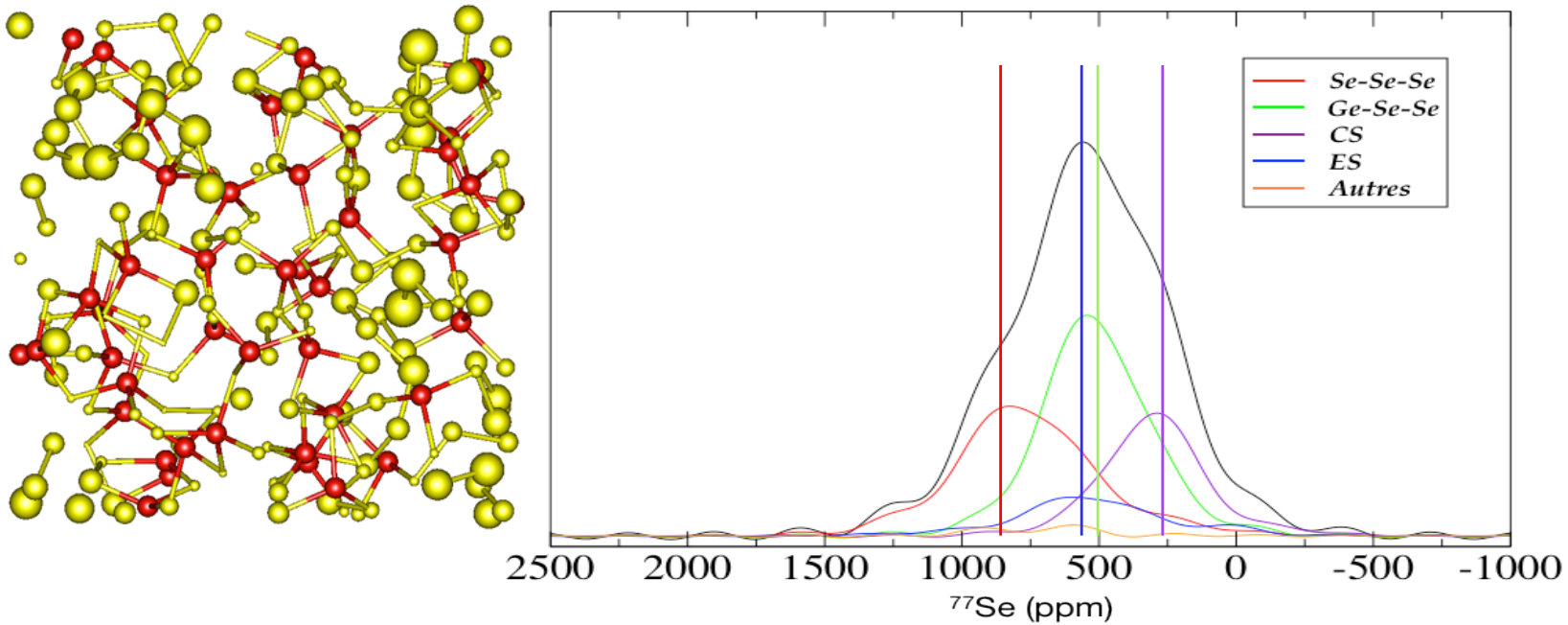
NMR spectrum has been simulated with the **Simpson** program*:

- emulate the experimental acquisition process
- takes into account the Chemical Shift **Anisotropy** and asymmetry parameters
- First, the CSA had been calculated with CASTEP for each Se of the MD box

***M. Bak, J. T. Rasmussen, N. C. Nielsen, *Journal of Magnetic Resonance* 2000, *147*, 296–330**



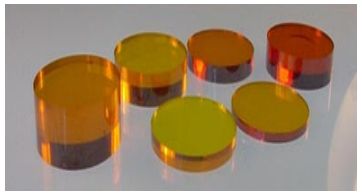
$GeSe_4$ NMR spectra reconstruction



Final MD box and ^{77}Se NMR (MAS 23 kHz) spectra **simulated** for an optimized configuration of the glass at 300 K

- the width of the signal is in fair agreement [~1000 ppm]
- the Se and $GeSe_2$ line positions are in good agreement with the experimental values
- the lineshape lacks the typical double peak feature found in the experimental spectra
- the large fraction of Ge-**Se**-Se units, resonating around 500 ppm determines almost entirely the lineshape
- the ES signal is also in that range (around 500 ppm), confirming CASTEP calculation on the crystalline β-$GeSe_2$ phase *(K. Sykina et al. **PCCP 2013**)* and disagreeing previous assignement*

*M. Kibalchenko, et al., *Journal of Physical Chemistry C* **2011** *115*, 7755–7759



$GeSe_4$ NMR spectra reconstruction from heterogenous starting configurations

PCCP

PAPER

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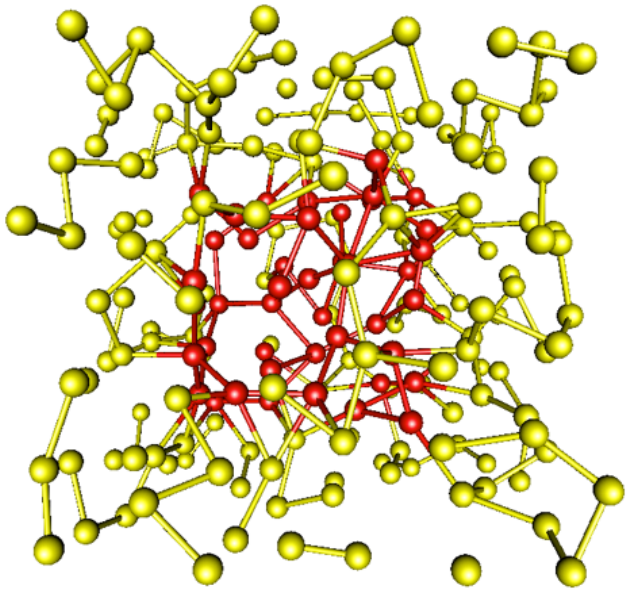
CrossMark click for updates

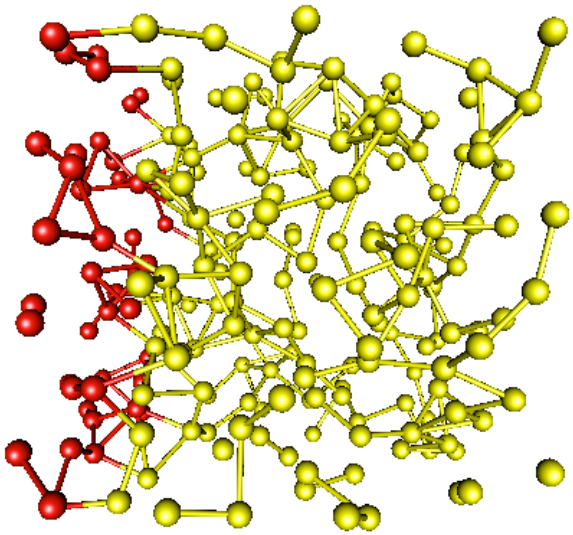
Cite this: *Phys. Chem. Chem. Phys.*, 2014, **16**, 17975

A combined ^{77}Se NMR and molecular dynamics contribution to the structural understanding of the chalcogenide glasses†

Kateryna Sykina,[a] Bruno Bureau,[b] Laurent Le Pollès,[b] Claire Roiland,[b] Michaël Deschamps,[c] Chris J. Pickard[d] and Eric Furet*[a]



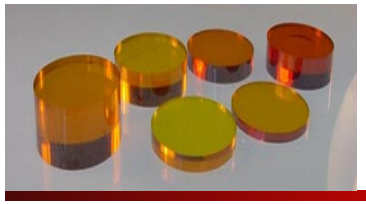
G for grain:
Germanium occupy a spherical volume



S for Slab:
Present a higher specific surface area

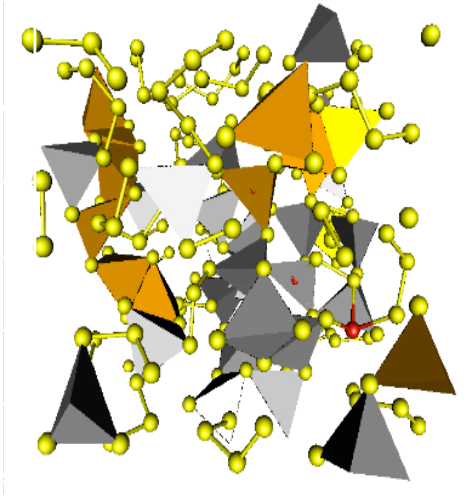
- experimentally powders of the raw materials are put together in the silica tube.

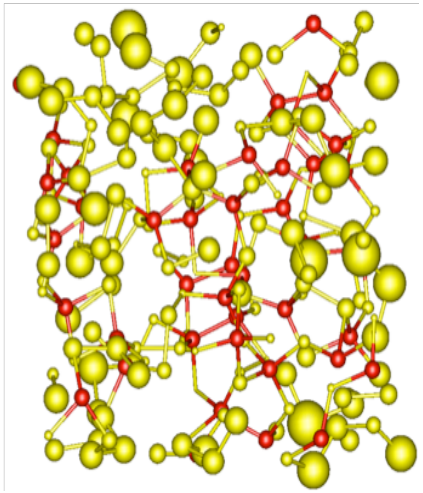
- Due to the large difference in the melting temperature between Ge (T_f = 1200K) and Se (T_f = 500K), a solid-liquid reactions promote the formation and linking of the $GeSe_4$ tetrahedra.



Let's go further to the $GeSe_4$ description

	H	S	G
Se-Se-Se	**29**	**35**	**38**
Ge-Se-Ge	**29**	**33**	**33**
CS	19	23	22
ES	10	10	11
Ge-Se-Se	**38**	**28**	**25**
Other	**~4**	**~3**	





From H (homogoneous) to S (Slab) and G (Grain):

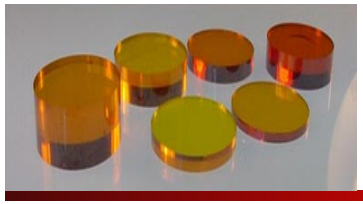
→ the **Se-Se-Se** and the **Ge-Se-Ge** rates **increase** *(+9% and +4%)*

→ the **Ge-Se-Se** rate **decreases** (-13%)

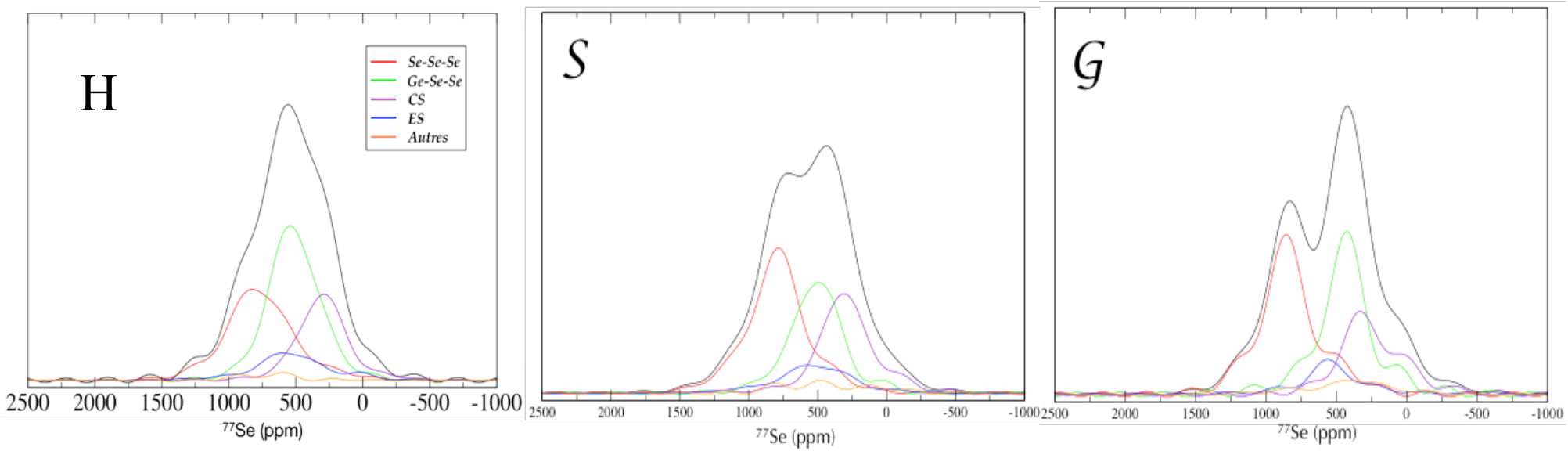
Nevertheless, pourcentages do not move dramatically and remain on the same range than those get on previous works …

(C. Massobrio PRB 2009, S. Sen et al JPCC 2010 and Edwards JNCS 2012)

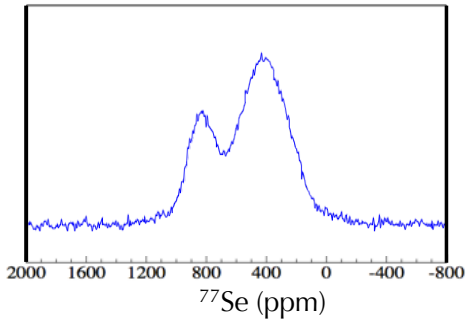
… is there any effect on the simulated NMR spectra ?



Let's go further to the $GeSe_4$ description

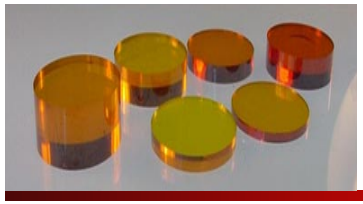


The simulated spectra obtained from the Grain MD file give a very good account of the experimental spectrum.



The evolution of the lineshape is partially due to the balance between the three kinds of Se neighborhoods, but mostly due to the anistotropy which shaped each individual line

→ difficult to anticipate the results without full calculation and simulation with CASTEP and Simpson



Conclusion on NMR

One has to be very carefull with longitudinal **relaxation effects**,

Difficult to anticipate and rationalise the **isotropic chemical shift** value of ^{77}Se

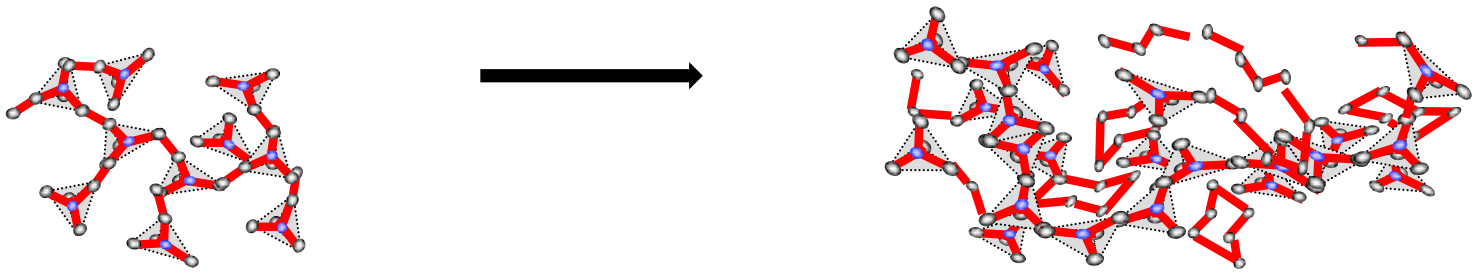
- Se chains and AsSe cages have the same CS on As_xSe_{1-x} (~800ppm)
- ES and Ge-Se-Se also on Ge_xSe_{1-x} (~500ppm)

Strong overlapping between the different contribution due to anistropic effects.

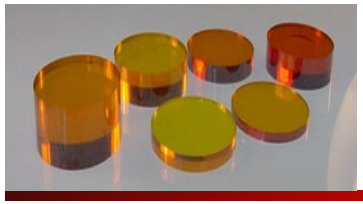
It is essential to carry out **full CS calculation** (iso and anisotropy) to simulate the experimental lineshape, even in glass.

Interestingly, the best result is obtain from the « Grain » MD file which correspond to the experimental condition of glass preparation.

The $GeSe_4$ structure contains about **33% of Se embedded in rings or chains**



Extended Se-n chains (**n > 3, up to n = 12**) are observed in the DM boxes



Conclusion on material sciences

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For As-Se glasses a clear **extremum is observed at r=2.4** (As_2Se_3) for all the physical properties.

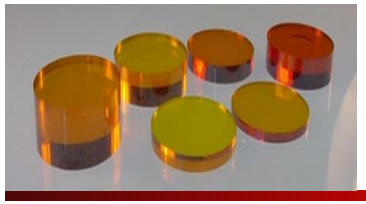
The physical properties transition are the direct consequences of the strong structural reorganisation.

For Ge-Se a **breaking point is observed at r=2,67** ($GeSe_2$). This observation could be connected with the emergence of direct Ge-Ge bonds beyond $GeSe_2$.

On the other hand, nothing special happens at r=2,4 ($GeSe_4$).

The physical properties are due to the **reticulation between the polyedra** rather than to r which corresponds the mean reticulation of each element.

Anyway $GeSe_4$ (for example) presents strong heterogeneïties, i.e. **weak VdW bonds**



Alternative way to prepare $GeSe_4$

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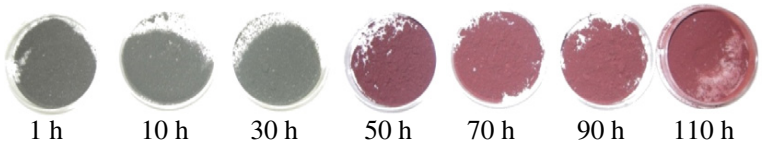
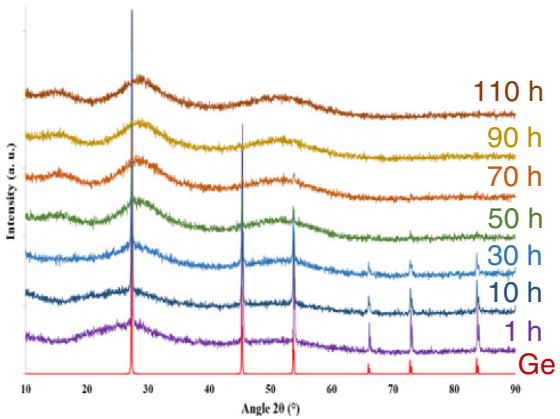
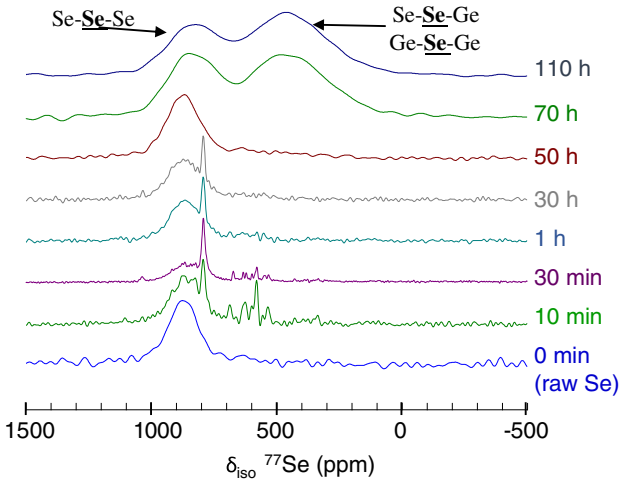
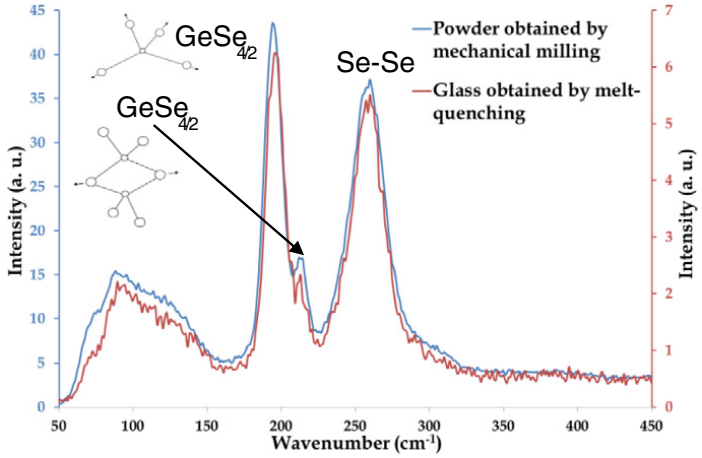
Structural study by Raman spectroscopy and ^{77}Se NMR of $GeSe_4$ and $80GeSe_2–20Ga_2Se_3$ glasses synthesized by mechanical milling

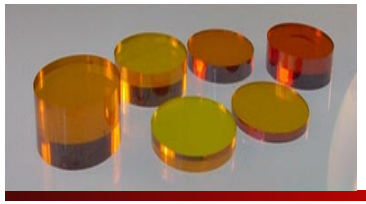
Elena Petracovschi [a], Bruno Bureau [a], Alain Moreac [b], Claire Roiland [a], Jean-Luc Adam [a], Xiang-Hua Zhang [a], Laurent Calvez [a,*]



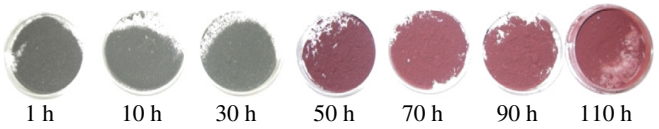


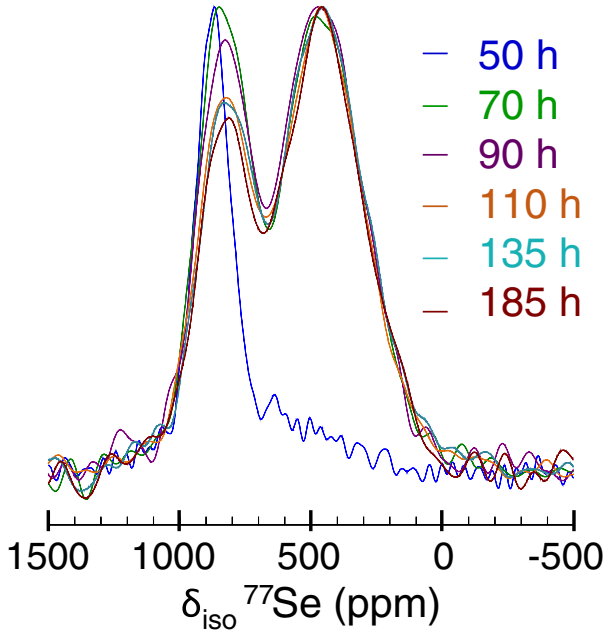




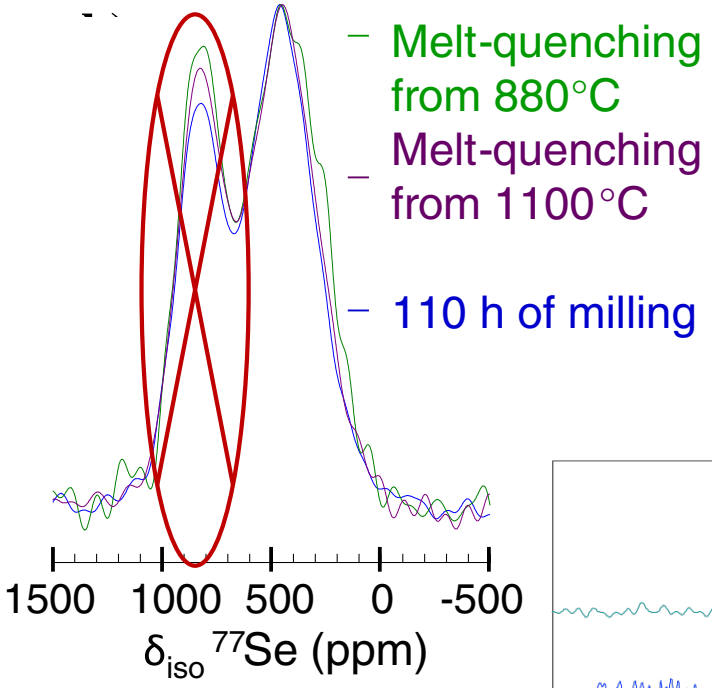


Alternative way to prepare $GeSe_4$

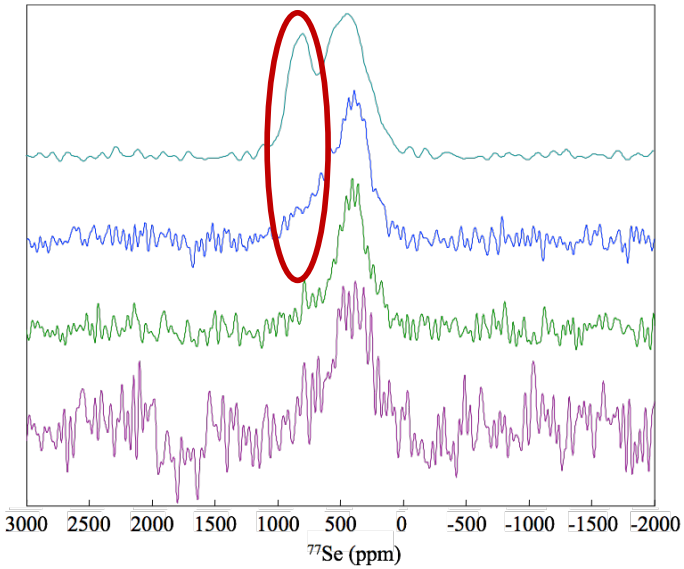




Melting and Quenching



$Ge_{20}Se_{70}Te_{10}$



Thank you for your attention

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